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Corrosion of Cermet Anodes During Low Temperature Electrolysis of Alumina

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Final Report

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ph
MASTER

Work Performed Under
Contract No. DE-FC07-89ID12848

Prepared for
U. S. Department of Energy

Prepared by
Aluminum Company of America
Alcoa Technical Center
100 Technical Drive
Alcoa Center, PA 15069-0001



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SUMMARY

Successful development of inert anodes to replace carbon anodes in Hall cells has the potential benefits of lower energy consumption, lower operating costs, and reduced CO₂ and CO emissions. Using inert anodes at reduced current density and reduced operating temperature (800°C) has potential for decreasing the corrosion rate of inert anodes. It may also permit the use of new materials for containment and insulation.

This report describes the fabrication characteristics and the corrosion performance of 5324-17% Cu Cermet anodes in 100 hour tests. Although some good results were achieved, the corrosion rate at low temperature (800°C) is varied and not significantly lower than typical results at high temperature (~960°C).

This report also describes several attempts at 200 hour tests, with one anode achieving 177 hours of continuous operation and another achieving a total of 235 hours but requiring three separate tests of the same anode. The longest run did show a lower wear rate in the last test; but a high resistance layer developed on the anode surface and forced an unacceptably low current density.

It is recommended that intermediate temperatures be explored as a more optimal environment for inert anodes. Other electrolyte chemistries and anode compositions (especially high conductivity anodes) should be considered to alleviate problems associated with lower temperature operation.

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OBJECTIVES

The broad objective of this cooperative agreement (DE-FC07-89ID12848) with DOE was to assess the commercial viability of using high surface area anodes (HSAA) and a low temperature electrolyte (LTE) in an aluminum reduction cell. The Phase I objective was to assess concept feasibility. The Phase II objective was to evaluate cell design concepts, and the Phase III objective was to determine at a high level of confidence if the technology is commercially viable.

Phase I results have been reported in several topical reports [1 - 4]. The following conclusions have been reached about the concept feasibility of the HSAA/LTE system from these studies:

1. A low temperature eutectic NaF/AlF₃ salt system (36 wt% NaF/64 wt% AlF₃ - 0.56 wt ratio) was found to be the best candidate electrolyte material.
2. The HSAA concept is not viable with the standard 5324-17% Cu Cermet anode material in the 36 wt% NaF/64 wt% AlF₃ (0.56 wt ratio) because of the low anode conductivity relative to the bath.
3. The corrosion of the Alcoa Cermet is very low in the 0.56 ratio bath. Cermet corrosion is influenced by the presence of carbon and sulfur.
4. The stability is poor in lithium containing salts.
5. The short duration of electrolysis tests and potential operating problems with the 0.56 ratio electrolyte system limit the confidence in the LTE system. In order to increase the confidence in the encouraging results of Phase I an extension, Phase 1A, was proposed.

The objective of Phase 1A is to determine the corrosion performance of 5324-17% Cu Cermet anodes in the low temperature eutectic NaF/AlF₃ salt system for longer duration (100 hour) laboratory electrolysis tests at higher currents. This report describes the results of these tests. The major topics include inert anode manufacturing, cell design and operating

procedures, and corrosion evaluation of Cermet anodes with a short discussion of issues for commercialization and recommendations for future work.

INTRODUCTION

The primary motivation for inert anodes is to replace carbon anodes in the Hall process to lower operating costs and energy consumption as well as reduce harmful carbon oxide, fluorocarbon and sulfur emissions, while maintaining present metal quality. From the very early work by Charles Martin Hall, it has been desirable to replace the consumable anodes with inert anodes.

In the Hall-Heroult process for the production of primary aluminum, carbon is an essential ingredient. Aluminum oxide is electrolyzed using a carbon anode in a cell containing a cryolite-based molten salt operating at temperatures of approximately 960°C. During the process, the carbon electrodes are consumed according the following reaction:



Although theoretically 0.33 Kg. of anode carbon is consumed for each kg of aluminum produced, nearly 0.5 kg is actually consumed due to additional losses due to air burning, and back reaction between aluminum and CO₂. To maintain purity of the aluminum product, only high quality petroleum coke is used.

The replacement of carbon anodes with inert anodes saves the energy content of the petroleum coke and eliminates the carbon oxide and sulfur oxide emissions. The carbon consumption for the U.S. Aluminum Industry is nearly 2.5 M. ton/year. In addition, inert anodes will eliminate fluorocarbon emissions which occur during anode effects (due to electrolysis of the cryolite electrolyte when the alumina content becomes too low). Inert anodes may improve productivity and efficiency because anode replacement will be less frequent allowing for more stable operation. Also, with more stable operation, it may be possible to reduce energy consumption through operating cells at lower current densities and/or smaller anode-cathode distances.

A low temperature electrolyte system is important for several reasons: (1) cell current efficiency is a well-known function of temperature, (2) it may permit use of new materials

for insulation and containment and (3) it is believed that the inert anode corrosion rate will be reduced at a lower operating temperature because of reductions in solubility of metal species and Cermet components.

One of the unique and more difficult operating characteristics of the Hall-Heroult process is containment of the electrolyte and metal in a frozen skull of electrolyte. Because of the corrosive environment of molten cryolite, a frozen layer of electrolyte must be maintained on the side-walls of the cell. This restricts the energy efficiency and limits cell design improvement because high heat losses are required to maintain the frozen side-wall. At lower temperatures existing materials for side-walls may exhibit sufficient chemical stability. These will be required for advanced cell concepts which require better insulating lining designs for energy conservation. Advanced cell concepts would be considered in Phase II of this program.

For Phase IA, we have used the eutectic NaF/AlF₃ (0.56 wt. ratio) salt exclusively because it has the advantages of low vapor loss and high alumina solubility relative to other low temperature salt systems considered. The disadvantages of low electrical conductivity and the potential to form hard cathode deposits were addressed in the test cell design.

Inert anodes have been the subject of many recent patents and publications [5-15]. The most notable development was the Alcoa Cermet anode developed during the Alcoa-DOE cooperative agreement #DE-FC07-80CS40158. This research was directed toward materials development, anode manufacturing, connection of the inert anode to metal current collectors, and evaluation of the anodes at Hall-Heroult cell conditions (1.10 wt% NaF/AlF₃ ratio, 960°C). The material developed under this contract is designated 5324-17% Cu Cermet. It was chosen as a basis for this study because it the most stable material tested to date and the focus of the program was to test the HSAA and LTE concepts not new anode materials. It is understood that this material may not represent the optimum formulation for the LTE electrolyte.

Major factors for the commercial viability of the HSAA/LTE process are the anode life, metal purity and production rates. The anode corrosion rate affects both the anode life and the metal purity. Excessive corrosion rates will contribute to reduced life as well as unacceptable metal purity. A preliminary economic assessment indicates that the Cermet material must corrode at less than 0.5"/year to achieve acceptable return on investment.

Since the Alcoa Cermet is comprised of oxides of nickel and iron in a copper matrix, these elements will contaminate the metal when the anode corrodes. Commercial metal purity requirements dictate maximum metal contamination levels of < 0.1 wt% Fe, <0.03% Cu and 0.03% Ni. In order to maintain cell productivity the anodes must operate at a superficial anode current density of at least 0.5 A/cm².

The focus of the Phase IA investigation was to:

1. Develop a cell design, standard practices, test procedures, and monitoring capabilities to operate bench scale tests of the 5324-17% Cu Cermet for 100 hours at the following conditions:

Alumina concentration	- Saturation
Ratio	- 0.56
Temperature	- 800°C
Current (Current Density)	- 7.5 A (0.5 amp/cm ²)

2. Assess the corrosion rate by dimensional change measurements and by material balances on metal pad pickup for a set of three (3) good anodes (verified by microstructural analysis) in 100 hour bench scale electrolysis runs.
3. Determine the microstructural changes in the three (3) test anodes tested above.
4. Make recommendations for future work.

ANODE FABRICATION AND CONNECTION TO COLLECTOR BAR

For the present evaluation, 5324-17 Cu Cermet anode composition developed during the earlier DOE program (DOE -FC07-80CS40158) and the present DOE sponsored program (DE-FC07-89ID12848) has been selected. The 5324 powder contains 51.7 w% NiO and 48.3 w% Fe₂O₃. Cu powder has been obtained from Alfa Ventron. The characteristics of Cu powder used in these tests are shown in Table 1.

Calcined and spray dried powder remaining from the previous program has been used for the present study. The flow characteristics of the spray dried powder permitted the anodes to be

fabricated into shapes without pressing flaws or laminations. It was previously demonstrated [16] that the spray dried powders can be easily mixed with various amounts of Cu or Ni powder and the resultant powder mixtures can be used to generate "graded connections" for Cermet to collector bar connections.

The anodes were 12.2 mm in diameter and the Cermet region was 96 mm long. The anodes were isostatically pressed in a rubber bag with approximately 70 gms of 5324-17 Cu powder. Four layers of graded composition containing 25, 50, 75 and 100% Ni and the balance Cermet were introduced on top of the Cermet powder. The topmost Ni layer was suitable for welded connections. Figure 1 shows the typical dimensions of the anode used for this study.

The anodes were pressed at 20,000 psi and sintered at 1350°C in an argon atmosphere. The sintering was carried out in a CM Inc. furnace, the Harrop box furnace or the Lindbergh tube furnace. No attempts were made to determine the oxygen content of the argon used in the studies with the CM furnace or the Harrop furnace. Anodes produced in these furnaces contained porosities in the range of 0.5-2.8% and also anodes showed various amounts of bleed out of the copper rich metal phase. It was, therefore, decided to sinter anodes in an argon atmosphere with carefully monitored and controlled amounts of oxygen. Also, a standard operating procedure was prepared to ensure uniformity and reproducibility of the anodes produced. A study on the effect of oxygen content of argon on the anode density, porosity, microstructure, and composition of the metal phase of the Cermet was also made. It was found that the porosity was not very significantly affected in the range of oxygen content studied. The density was about 6.05 g/cc when sintered in argon containing 70-150 ppm oxygen. The majority of the anodes were sintered in an atmosphere containing argon with 70-150 ppm oxygen. These anodes were sintered in the Lindbergh furnace. The actual density of the fabricated anodes was about 6.5 g/cc because these anodes contained a graded connection which included additional amounts of metallic Ni. The details are shown in Figure 1 and Table 1.

Table 2 and Figure 2 show the effect of oxygen concentration of the argon gas on the density and porosities of the anode. Table 3 shows the effect of oxygen concentration of the gas on the composition of the metal phase of the Cermet for several important runs.

Table 1

Physical and Chemical Analyses of Cu Metal Powders

Supplier	Alfa
Designation	10 μ m
Particle Size μ m	
90% less than	27.0
50% less than	16.2
10% less than	7.7
Spectrographic Analysis ^(a)	
Element, wt%	
Ag	.00
Al	.00
Ca	.02
Cu	Major
Fe	.01
Mg	.01
Ni	nd
Pb	.30
Si	.01
Sn	.30
Zn	nd

^(a)Note: Values accurate to a factor of 3.

Table 2

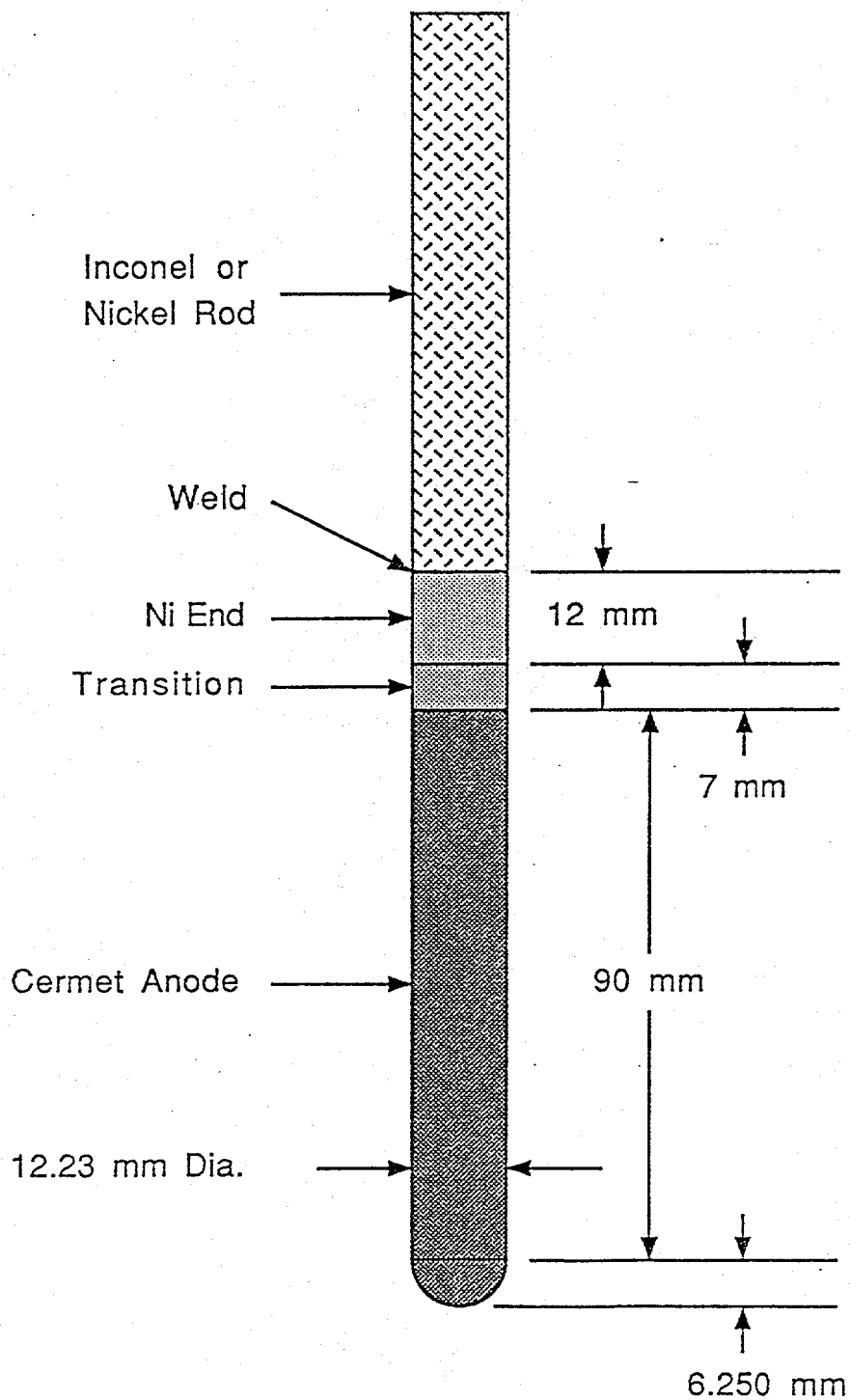
Oxygen ppm vs. Poros. and Dens.

<u>S#</u>	<u>PPM O2</u>	<u>Poros.</u>	<u>Avg. Poros.</u>	<u>Dens.</u>	<u>Avg. Dens.</u>
S# 692867	350	0.133	0.133	5.998	5.998
S# 692865	250	0.133	0.133	6.019	6.019
S# 579647	150	0.121		6.033	
S# 579646	150	0.149	0.119	6.051	6.045
S# 579644	150	0.086		6.051	
S# 579643	90	0.068		6.053	
S# 579640	90	0.144		6.046	
S# 579639	90	0.071		6.059	
S# 579637	90	0.145	0.116	6.048	6.050
S# 579636	90	0.145		6.044	
S# 579635	90	0.082		6.058	
S# 579634	90	0.141		6.043	
S# 579633	90	0.130		6.053	
S# 579632	75	0.160	0.149	6.045	6.046
SE 579631	75	0.138		6.047	
S# 579628	70	0.117		6.043	
S# 579627	70	0.105		6.037	
S# 579626	70	0.097		6.043	
S# 579623	70	0.032	0.088	6.056	6.048
S# 579622	70	0.099		6.050	
S# 579621	70	0.074		6.048	
S# 579620	70	0.093		6.057	
S# 579612	19	0.051		5.937	
S# 579610	19	0.611	0.300	5.911	5.926
S# 579611	19	0.239		5.929	
S# 579616	17	0.070		5.918	
S# 579615	17	0.108	0.069	5.948	5.922
S# 579614	17	0.028		5.964	
S# 579613	17	0.068		5.859	

Table 3

Metal Phase Analyses vs. O₂

	Run #	ppm O ₂	Surface			Interior			Initial		
			Cu	Ni	Fe	Cu	Ni	Fe	Cu	Ni	Fe
C1410	29	90	80.3	18.7	1	75	23	1.7	78	20	2
C1226	8	--	97.5	0.7	1	83	18	1.8	82	17	2
C1401	27C	90	86	14.2	1	78	21.7	0.7	80	18	3
C1402	28A	90	77	22	1.8	78	21	1.2	78	20	3
C1403	28C	90	73	25	2.4	77	22	1.7	81	18	2
C1308	25B	70	84	14	2	81	18	1	79	19	2
C1326	27B	90	78	20	2	76	22	2	80	18	2
C1325	23	70	66	29	5	81	18	1	80	19	2



Inert Anode Geometry

Figure 1

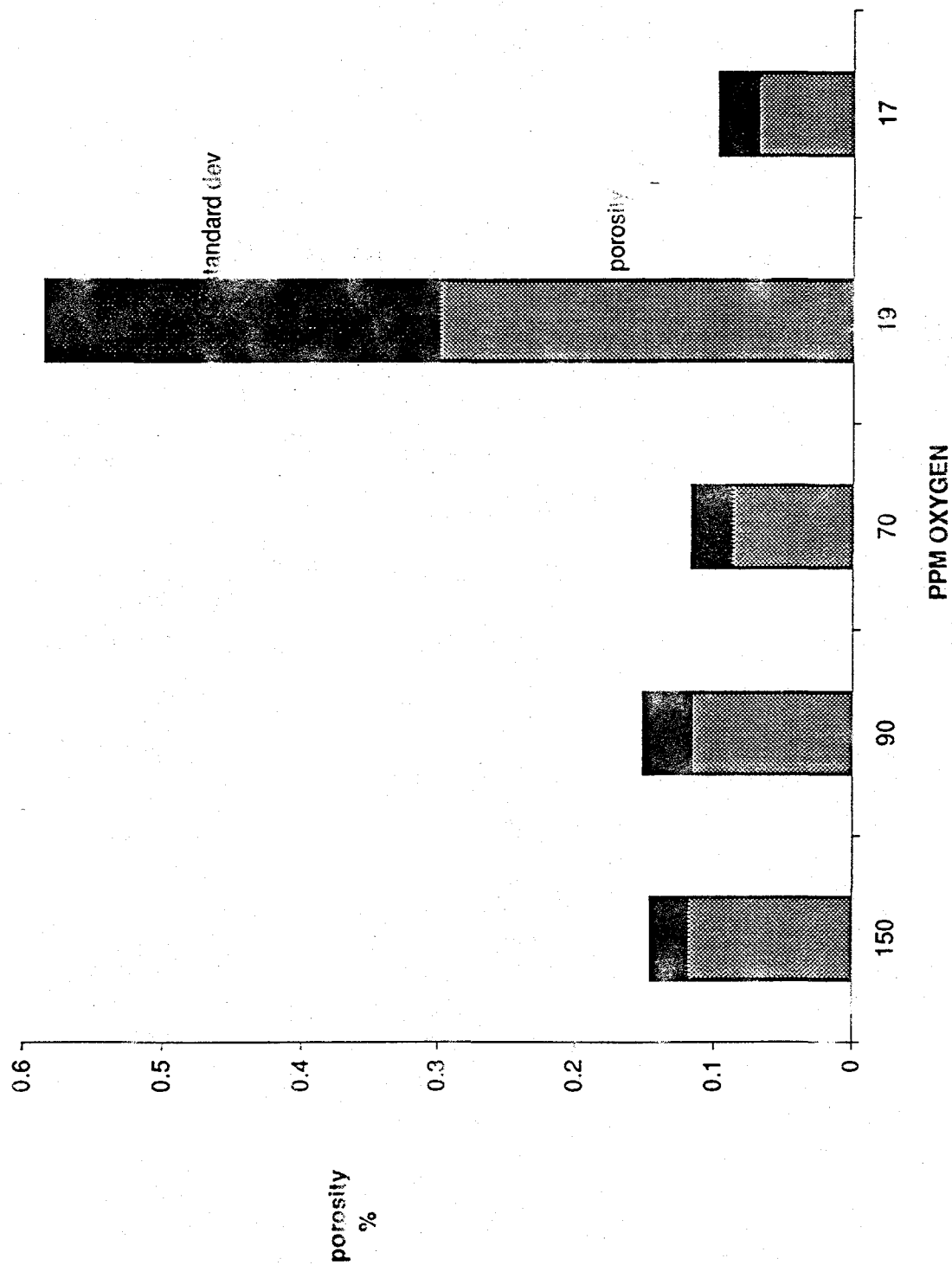


FIGURE 2

Porosity of Cermet Anode Versus Oxygen Contents of Argon Gas

CELL DESIGN

The focus of the bench cell design was to develop a design capable of reproducible cell operation for 100 hours to evaluate corrosion performance of Cermet anodes. To achieve this goal, the following guidelines were used:

- Alumina saturation will be maintained by means of semicontinuous feeding with good bath circulation to rapidly dissolve alumina feed. An accurate volumetric feeder system with a small shot size was developed for the bench cell. Good bath circulation is achieved by bubbling argon through a bed of tabular alumina. All materials in direct contact with bath except the anode are high purity alumina.
- Aluminum carbide formation will be minimized in the bath by eliminating direct contact of bath with carbon. This can be achieved by the use of alumina liners
- A metal pad will be provided to obtain material balance on impurities from the anode. This requires maintaining a small enough metal pad to obtain a measurable change in impurity levels during a run. Metal pad mass can be reduced by displacing much of the cathode volume with the alumina bubbler system.
- Automated 24 hour operation will be provided with minimal operator attention. Computer control features are cell current control, automated purge to unplug bubbler, automated volt-amp curves, automatic data logging, telephone call out during off hours upon extended bubbler alarm conditions, and safeguards for computer failure or power failure.

The basic cell construction is shown in Figures 3 - 5. A distinguishing feature of the cell is the alumina crucible and bubbler system located in the center of the cell. This serves several functions. First it provides a source of alumina to help maintain alumina saturation. Second, the cup contains a supply of fresh alumina for the cell to avoid overfeeding and to minimize muck formation below the metal pad. Third, the argon bubbler system helps to circulate bath to improve the dissolution rate of the alumina being fed to the cup. Fourth, the crucible displaces a substantial volume of the metal pad. A smaller volume of metal increases the

precision of the material balances for copper, nickel and iron contamination from the inert anode.

An argon bubbler and alumina crucible arrangement is used to provide a well mixed sink for dissolving alumina. Two different arrangements were used. The first, illustrated in Figures 3 and 4, uses four alumina tube downcomers to transport bath down to the base of the bed of fine tabular alumina. The downcomer arrangement is shown in Figure 4. The argon purge gas exits the bubbler tube at the bottom center of the crucible. The rising gas bubbles will entrain bath and carry it vertically through the bed of tabular alumina and undissolved alumina particles resting on top. In the second arrangement, shown in Figures 5 and 6, the downcomers were replaced by using large diameter tabular alumina balls. Figure 7 shows the lid design used for a typical test.

The use of a reference electrode is important to differentiate between processes occurring at the anode or cathode. The reference electrode is shown in Figure 8. It is designed to give a stable reference potential close to that of the aluminum metal pad. The present design has evolved over years of bench cell research. The basic design was modified slightly by increasing the diameter of the tungsten rod and the alumina sleeves to provide increased life for a 100 hour test. The electrolyte composition in the reference electrode is the same as for the bath for each run.

Bench Test Cell for Cermets Anodes

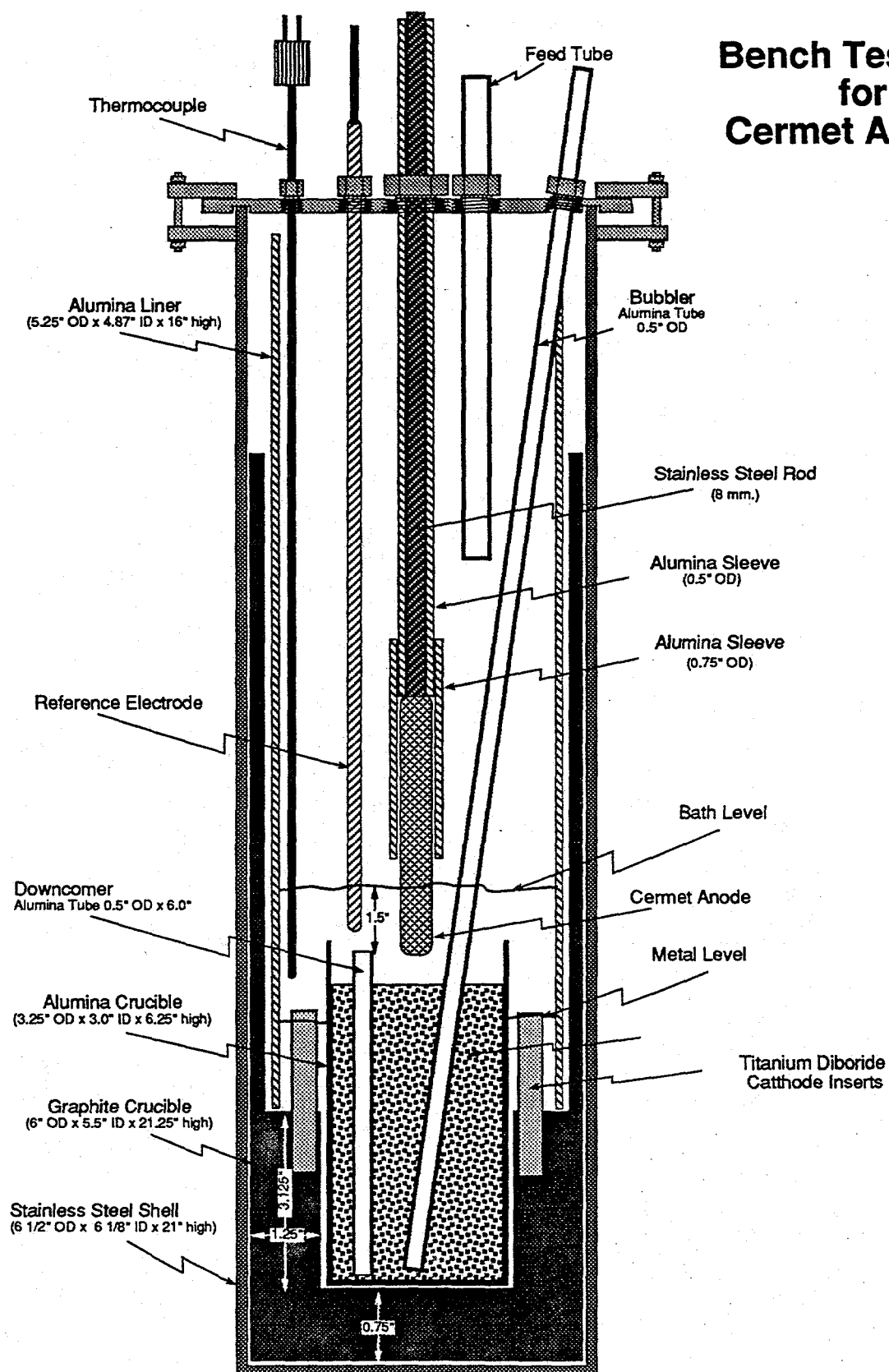


Figure 3. Side View

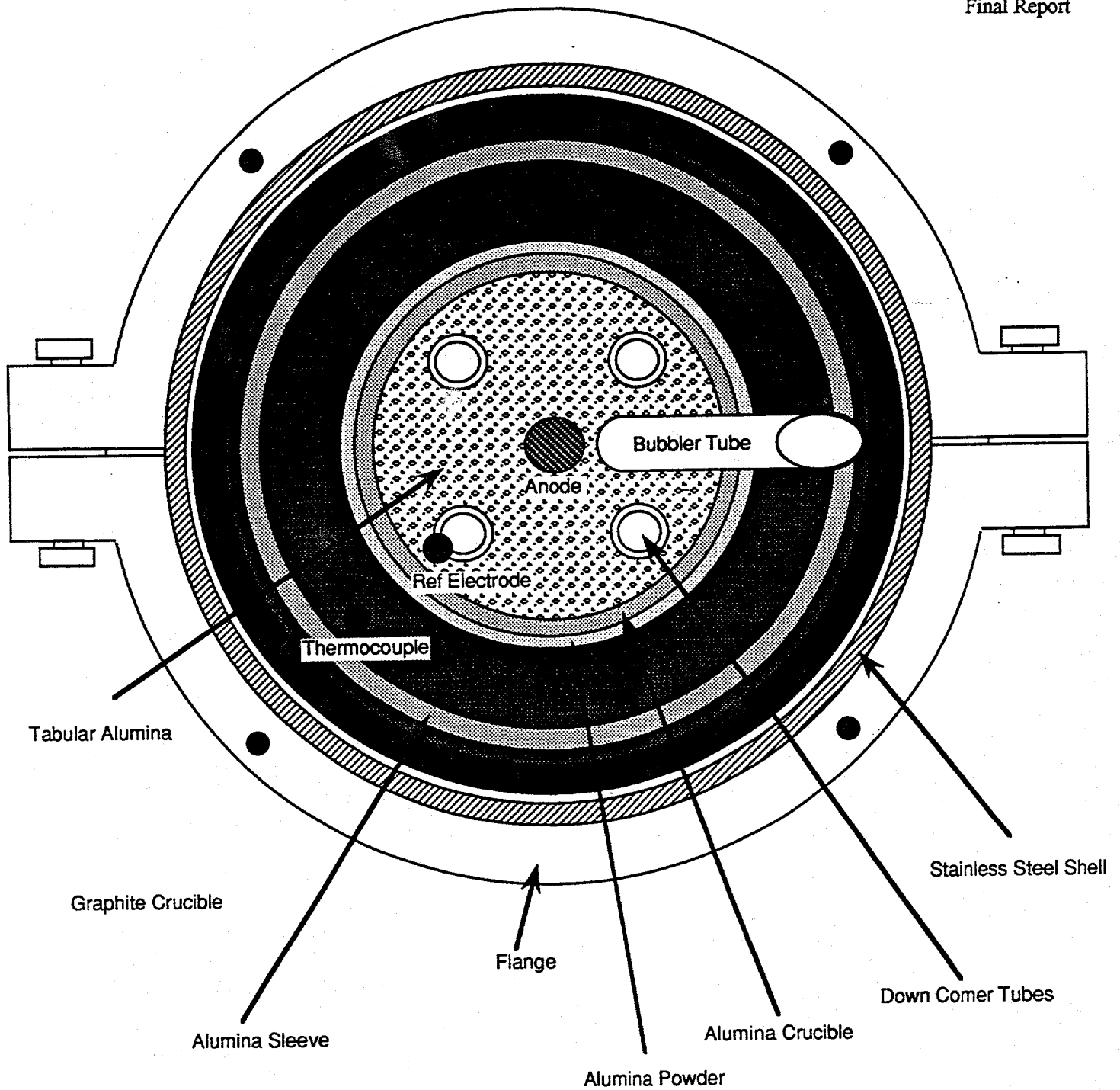


Figure 4

Bench Cell - Top View

Tabular Alumina

Bench Test Cell for Cermets Anodes

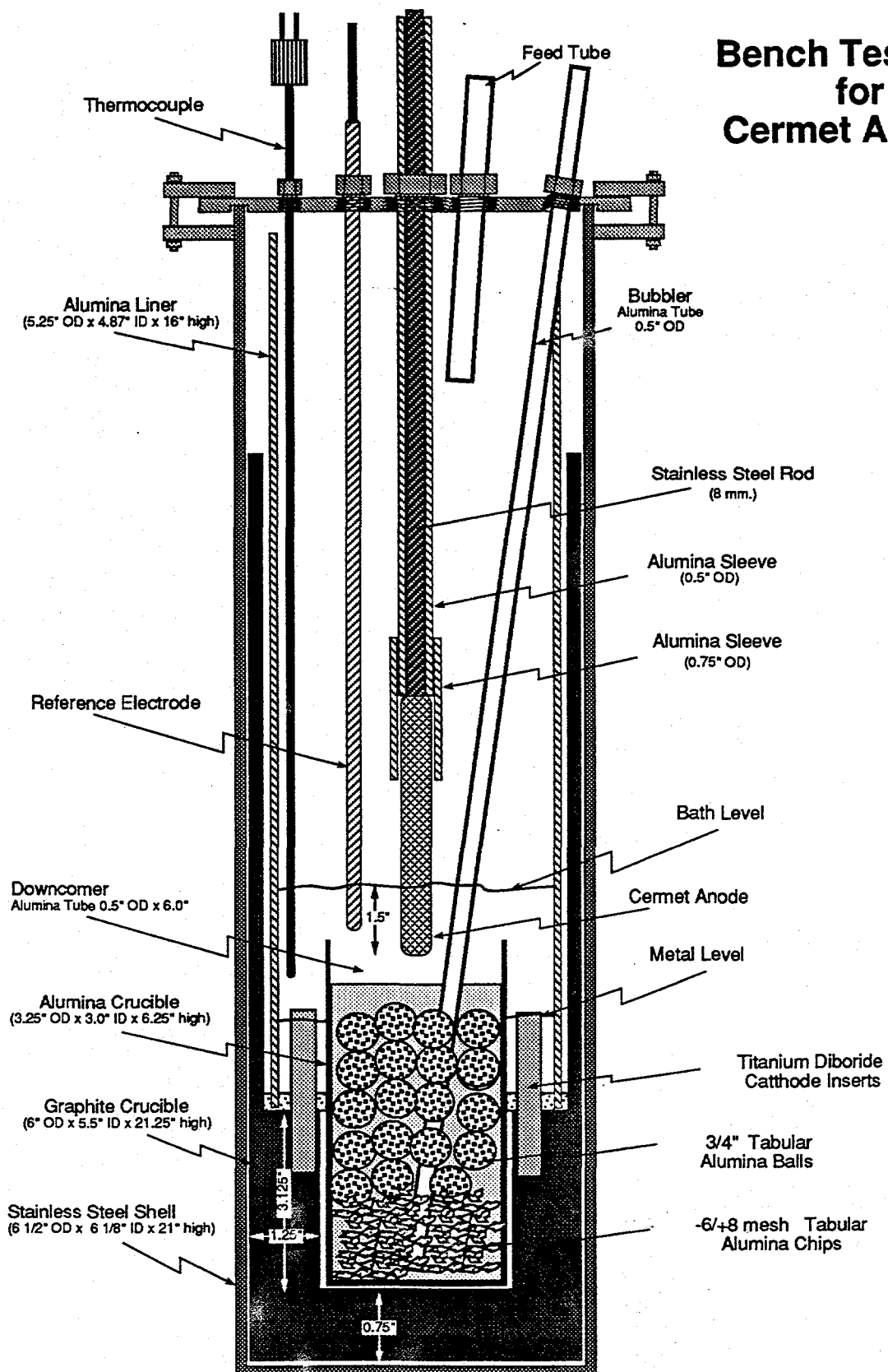


Figure 5

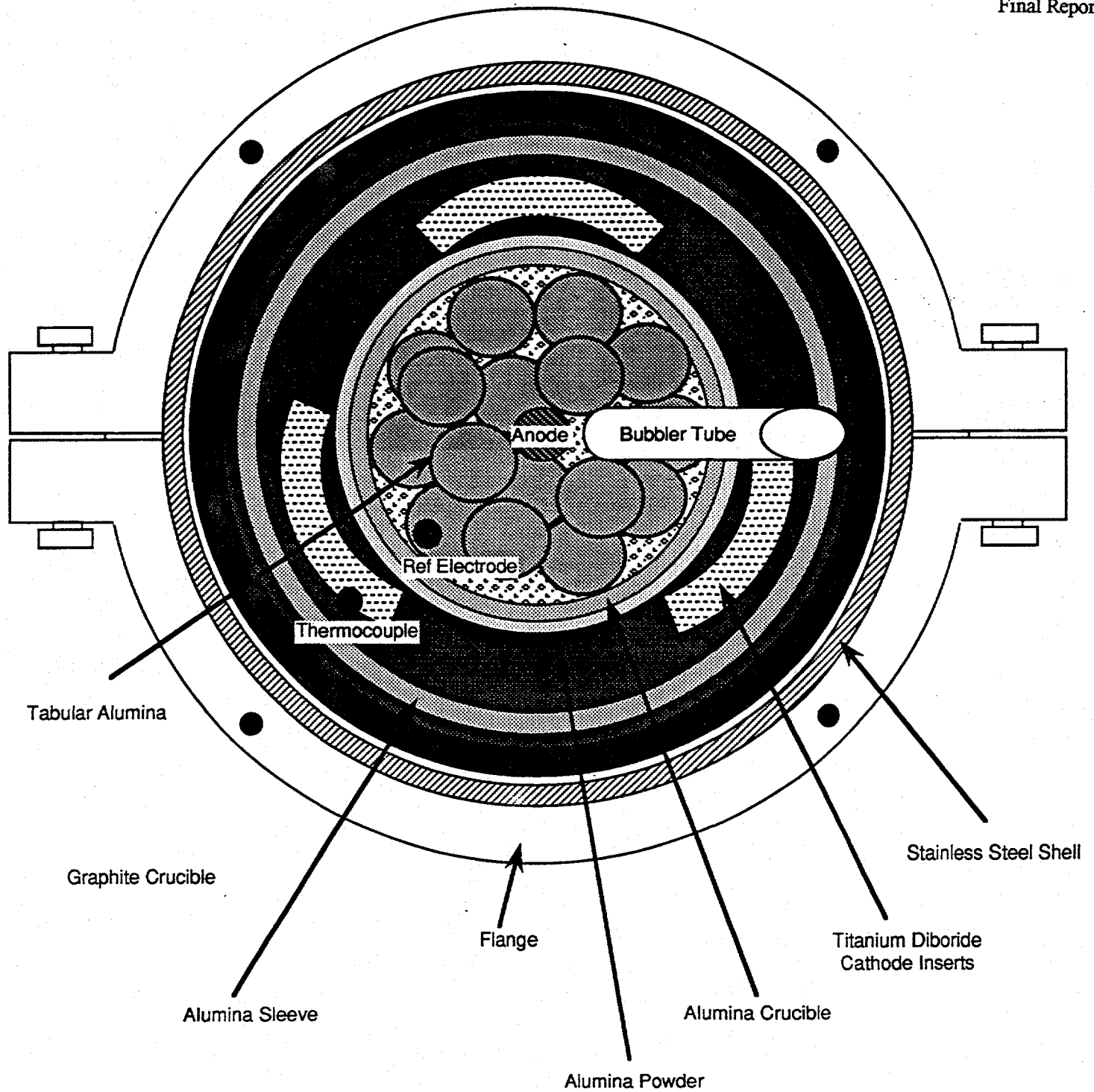
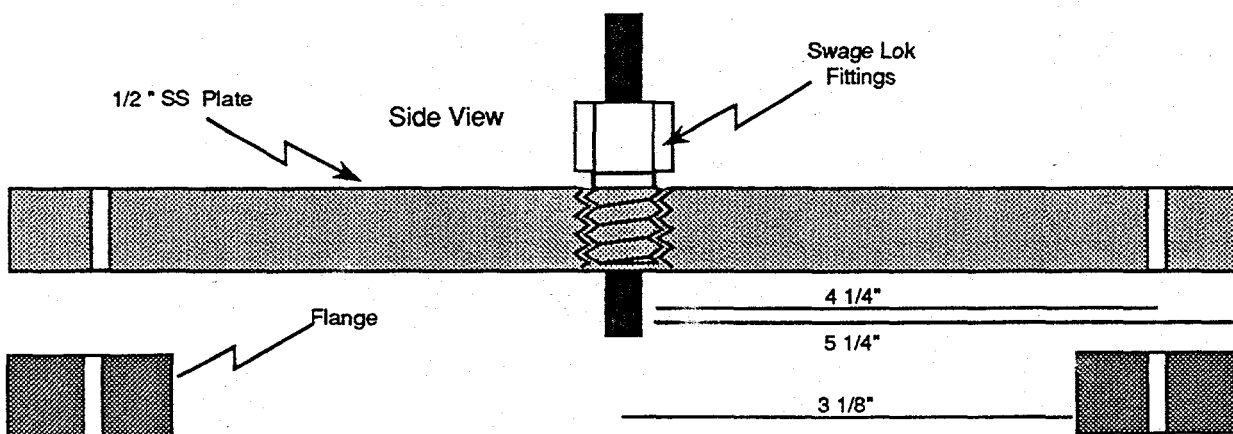
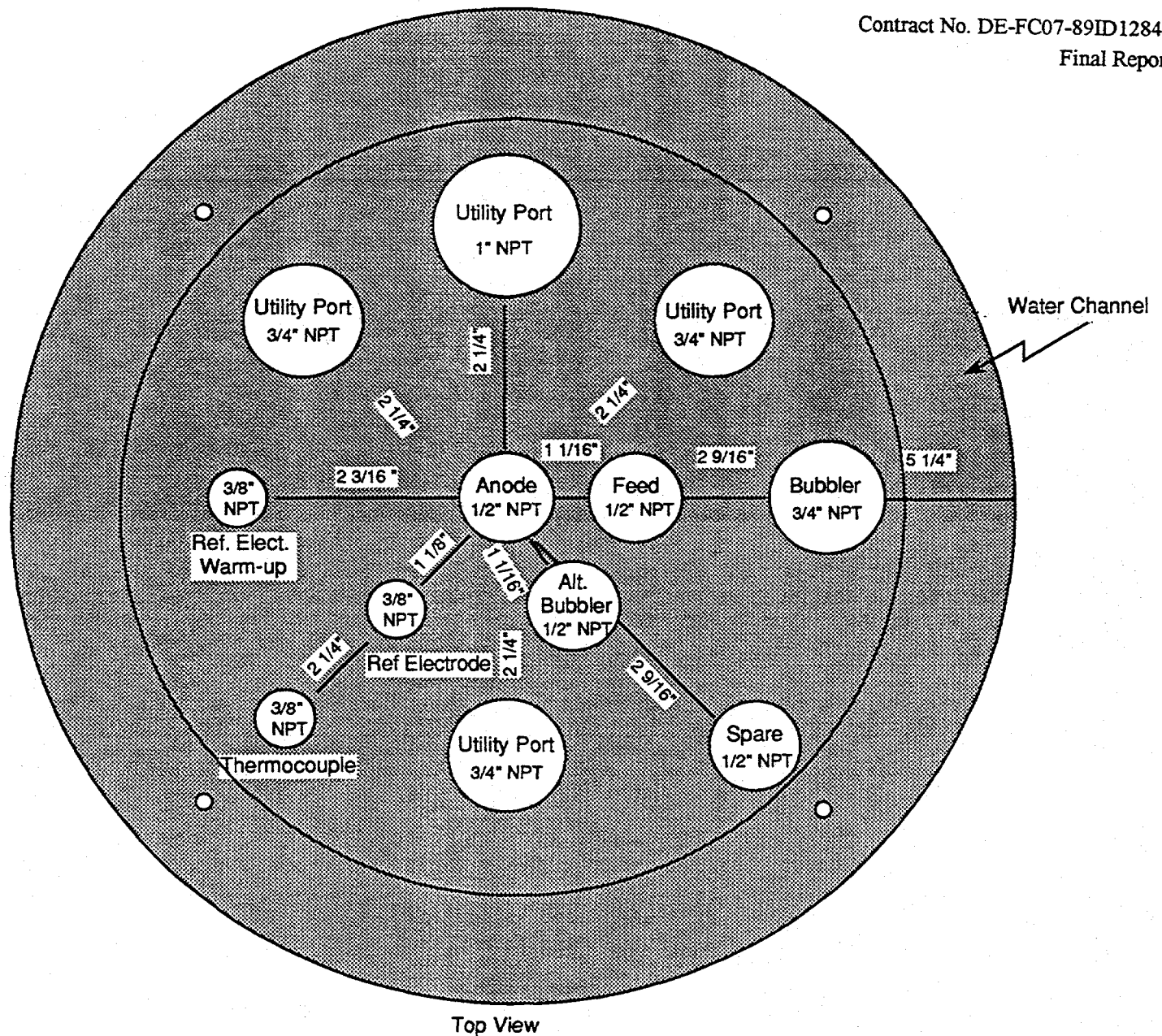


Figure 6

Bench Cell - Top View



High Temp. Bench Cell Lid Arrangement

Figure 7

Not To Scale

All Dimensions are Radial Position to Center of Lid

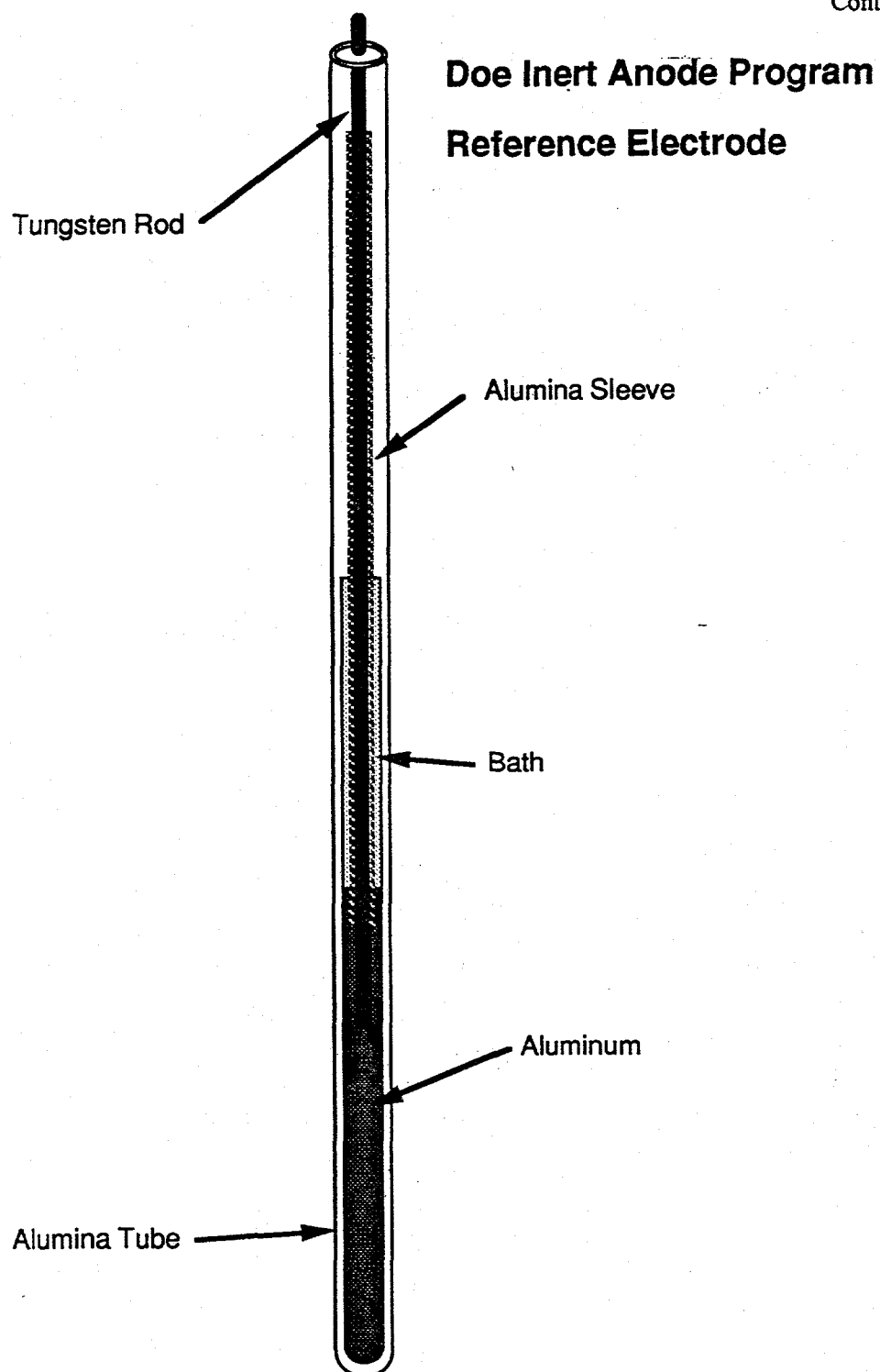


Figure 8

A very simple volumetric feeder was developed to deliver small uniform shots to the cell. The unit basically consists of a feed hopper, volumetric chamber, argon purge, and feed delivery tube. The feeder is controlled by a solenoid activated air actuator system. The solenoids are activated by either external timers or by the computer system. The feed hopper consists of a plastic funnel with a lid cemented on it. The hopper can be purged with argon for feeding dry alumina.

The volumetric chamber consists of a stainless steel ball valve with one side of the ball plugged. By controlling the plug length it is possible to change the volume of the chamber. The unit is presently set to deliver approximately 1.0 gram of alumina per shot. The entire feeder assembly can be removed from the cell to check the weight of feed delivered to the cell. The feed amount is very repeatable with less than 0.5% deviation per shot.

Anode protection above the bath is provided by an alumina sleeve which fits over the welded connection area and down on the anode as shown in Figure 3. The sleeve should not extend into the liquid bath zone as it has been observed that accelerated corrosion of the anode will occur under the sheath.

The furnace is a custom fabricated electrical resistance design utilizing nichrome heating elements with AC power. West 2050 digital temperature indicators and controllers are used to control temperature and sense bath and furnace temperature. Temperature sensing is by an alumina-sheathed type K thermocouple in the electrolyte.

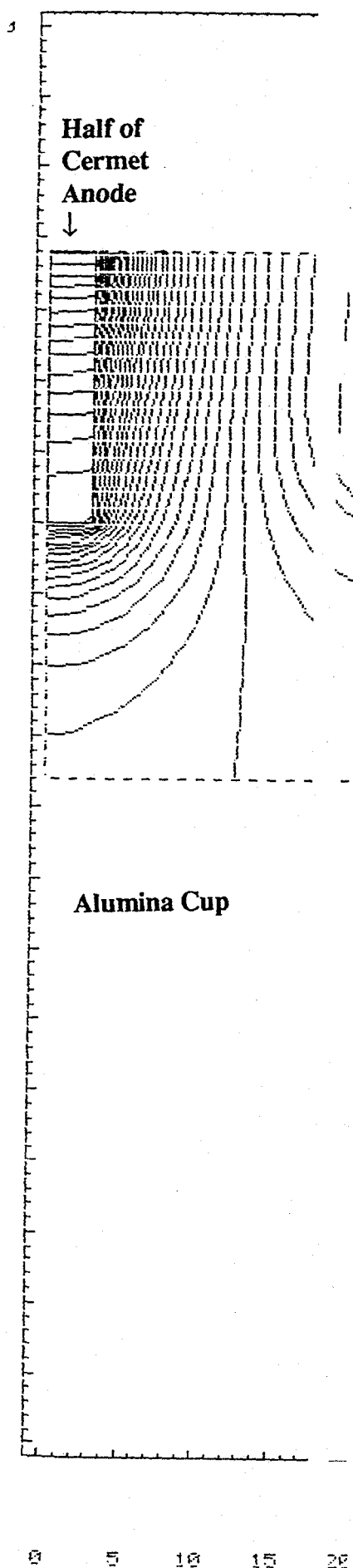
DC power is provided by a KEPCO power supply with a maximum rating of 10 Amps at 7.5 volts. Signal and power connections are made using type T160S alligator clips.

The non-ohmic voltage drops in the cell are measured by the voltage interrupt technique using an Schrieber and Associates IR switch set for a 40 ms interrupt. This instrument measures the voltage between the working electrodes and the reference electrode before and after the interrupt. The IR (ohmic voltage drop) is determined from the difference in the two voltages. By alternating the working electrode between the anode and cathode, both the anode and cathode overvoltages were measured separately.

The construction materials in contact with the electrolyte were selected to avoid the influences of impurities on anode corrosion. Materials in direct contact with the electrolyte include the Cermet anode, alumina liners and sleeves, high purity aluminum, titanium diboride cathode, tungsten measuring rods and argon purge gas. The main components are graphite in a stainless steel retort. Direct contact of graphite and the electrolyte is avoided by an alumina sleeve or the metal pad.

The cell was designed to provide a nearly uniform primary current distribution on the sides of the anode. A potential map is shown in Figure 9. Figure 10 shows the current density on the anode surface. The general cell arrangement and the anode surface current from the side of the anode resulting in an anode current density which is nearly uniform relative to a typical lab cell. At 1.5" immersion at 7.5 amps operation, the anode current density is 0.5 amps/cm^2 . With this design, the cathode current density ranges from 0.38 amp/cm^2 to 0.68 amp/cm^2 .

Titanium diboride inserts were later installed in the cathode to provide a better electrical connection between the metal pad and the graphite. The basic layout is shown in Figure 11. The primary current distribution for this modification was not modeled.



Low Temperature Smelting

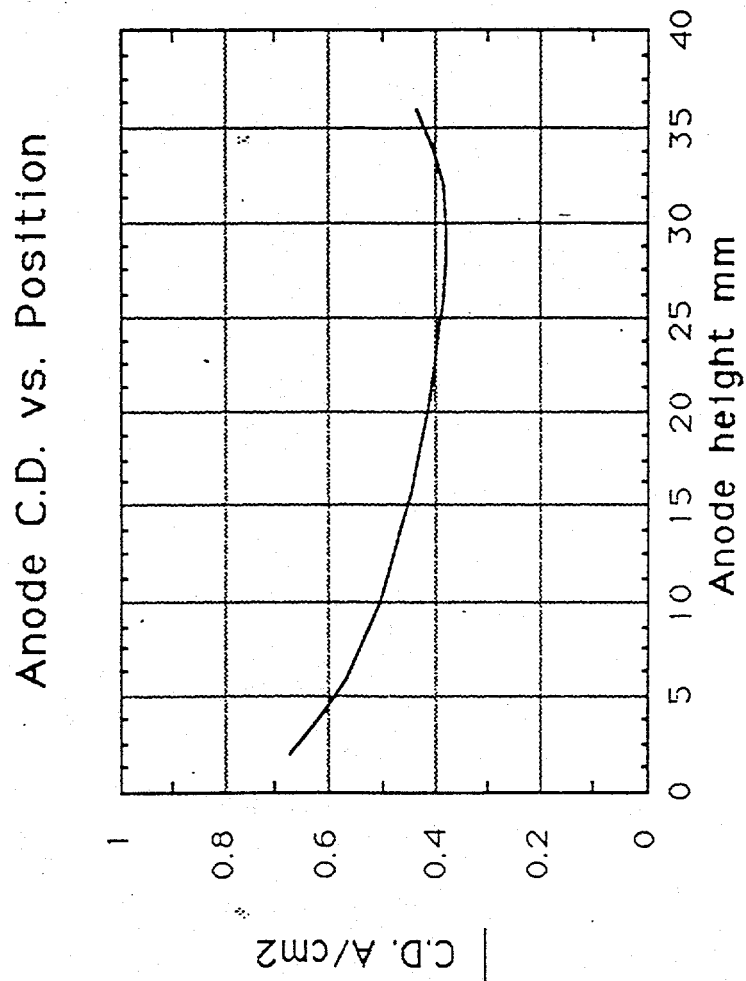


Figure 10 Anode Current Density (CD) Versus Position

CELL OPERATION AND START-UP

Standard operating practices were developed for the cell preparation and start-up in order to reduce variability from run to run. These are listed in Appendix II. In general the cell was charged with the metal and electrolyte and heated to the operating temperature at a rate of 100°C/h under an argon purge. After the cell was at operating temperature, the reference electrode was introduced and the anode was slowly lowered into the cell at a rate of approximately 1"/min until it was at the proper immersion depth. Then the computer program would be started and electrolysis would proceed under computer control.

Table 4 below lists the operating targets for the 100 hour runs.

Table 4
Bench Cell Operating Setpoints

Temperature	800°C
Bath ratio (wt)	0.56
Current	7.5 Amps
Anode Immersion	1.5"
Current Density	0.5 amp/cm ²
Alumina Conc.	Saturation ~4.2%
Alumina Feed Rate	0.637 g/A-hr
Bath Level	1.25" over alumina crucible
Bubbler Flow Rate	1.0 SCFH

During steady operation, the cell was operated under computer control. The computer controlled cell current, alumina feed additions, IR meter switching, and bubbler gas flow. Routine manual operations included determination of anode immersion depth, bath and metal levels, adding make-up bath, running volt-amp curves, feeder calibration, taking electrolyte and metal samples, and visual observations. Every 24 hours the amp-hour readings feeder shot counts and bath and metal additions and subtractions were logged. In addition to logging the fifteen minute averages of the variables listed in Table 5, the computer would alarm abnormal conditions such as bubbler tube plugging, high IR readings, bad reference electrodes, etc.

Table 5
Computer Logged Data

Cell volts
Amps
Amp-hours
Anode-to-reference voltage
Cathode-to-reference voltage
Anode IR
Cathode IR
Anode overvoltage
Cathode overvoltage
Total feed shots

Scan frequency = 10 sec

Logged average every 15 min.

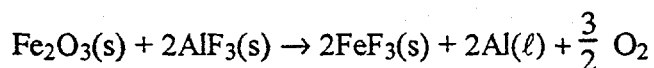
ANODE CORROSION MECHANISMS

The rates of all thermally activated processes decrease with a decrease in temperature. The solubility of iron and nickel oxides in cryolite melts was found to decrease with a decrease in temperature and bath ratio in previous experiments carried out in this laboratory. The major thrust of the present program was to determine the feasibility of operating low temperature, low ratio bath and maintain low anode deterioration rates. It has been found that under the best operating conditions the anode corrosion rate is low but the anode still introduces undesirable quantities of impurities in 100 hour tests.

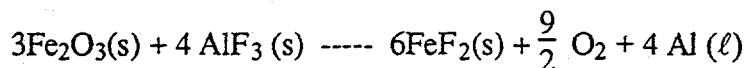
The $\text{NiFe}_{2+x}\text{O}_4\text{-Ni}_{1-x}\text{O-Cu}_{1-x-y}\text{Ni}_x\text{Fe}_y$ Cermet anodes may deteriorate in operating Hall cells by a number of possible mechanisms.

- Reduction of the anode by dissolved metal species

The soluble metal species in the melt may come in contact with the anode and reduce the oxide component resulting in a degradation of the anode. This mechanism may be



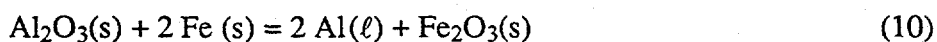
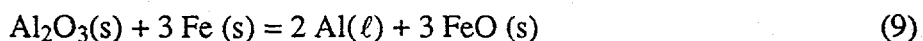
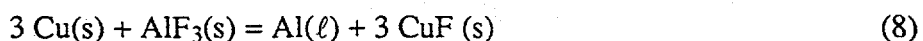
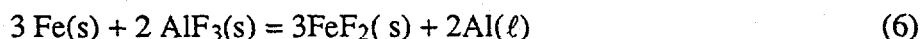
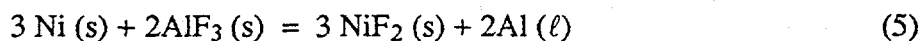
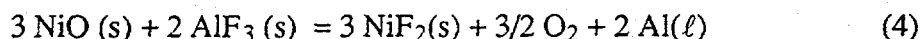
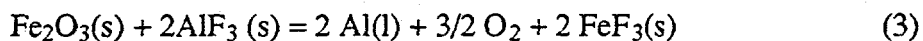
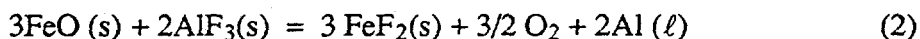
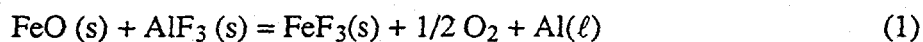
with a decomposition voltage of 2.483 with a unit activity of Fe_2O_3 and with an AlF_3 activity of .01 at 1073K or

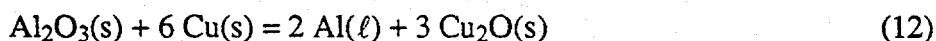


with a decomposition voltage of 2.626 at unit activity of Fe_2O_3 and AlF_3 activity of 0.01 at 1073K.

A set of possible competing reactions are shown below:

Reactions





It can be seen that under certain conditions some of these reactions may compete with the desired electro-chemical reaction for producing oxygen at the anode and Al at the cathode. These undesirable reactions lead to anode deterioration. It is apparent that when Al_2O_3 concentration is significantly below saturation, the anode deterioration through reactions 1-8 would be significantly higher because competing reactions can become more favorable compared to the desired reaction. The low Al_2O_3 concentration was associated with poor anode performance in all these studies.

- Dissolution of anode components into the electrolyte and reduction by molten Al

The oxide components of the anode NiFe_2O_4 and NiO are soluble in the electrolyte. The solubility limits of such oxides are low; but their dissolution and rates of dissolution may determine the corrosion of the anodes. The solubility limit determined in the 1980-1985 Alcoa-DOE cooperative program was 0.1 wt% Fe for Fe_2O_3 and 0.025 wt% Ni for NiO . The solubility limit decreases with decreasing temperature and increases with decreasing Al_2O_3 concentration. If the dissolved oxide is reduced immediately and effectively, the dissolution will continue even though the solubility limit may be low. Thus, the cathode area and metal solubility may be important factors in the rate of anode corrosion.

The dissolution of the anode components might take place heterogeneously. For example, the anode might be attacked preferentially at the grain boundaries and grain fall out may result. The material will eventually get reduced and end up contaminating the metal. In the present experiments this situation was found to be present.

In these experiments, the cathode area was significantly higher (anode area to cathode area was about a factor of 20) than commercial cells (anode area to cathode area about 1:1.2). If the reduction of dissolved oxide at the cathode is the rate determining factor, significantly higher corrosion may be expected with large cathode area. On the other hand, the anode corrosion may be reduced by decreasing the cathode area. In the present experiments, the mass transfer in the electrolyte was very high because of bubbling of

argon. The concentration of Fe and Ni oxides was always low at less than 0.01 indicating the rate of reduction of dissolved oxides to be extremely high. It appears that this mechanism of corrosion involving dissolution of oxides and reduction at the cathode is operative in all test runs to some extent.

RESULTS AND CONCLUSIONS

Anode corrosion due to chemical dissolution is minimized when the bath is saturated with oxide. Therefore, it is desirable to maintain alumina saturation throughout the entire course of a run. The oxide content of the bath was monitored periodically by sampling and determining the total oxygen content by the LECO [17] method. The saturation value for the LTE electrolyte was determined by two different methods. The first was based on weight loss from a rotating high purity alumina disk and second was based on overfeeding the cell and allowing it to equilibrate over time. The saturation value obtained by both methods was 4.05 to 4.5% alumina based on the LECO method. The best estimate is 4.05 - 4.15%. This is a much higher solubility than was initially estimated for this salt system but is consistent with values recently reported by Pankov, et al. 1991 which indicate that the solubility is in the range of 3 - 5%.

As was mentioned above, it is desirable to maintain alumina near saturation throughout the entire course of a run. We attempted to achieve this condition through a combination of means.

1. Cell design: A cell was used with a very large bath capacity which is initially saturated with alumina. All materials in direct contact with the bath except the anode and the metal pad were made of alumina. A bubbler was used to provide agitation to assist dissolution of added alumina. A feeder system was designed and used with a small shot size for semicontinuous feeding of alumina.
2. Cell operation: We initially saturated the bath with alumina by adding alumina to the cell without electrolysis. We fed stoichiometrically excess amounts of alumina (assuming 100% current efficiency). We gravimetrically monitored the amount of alumina fed to the cell. We monitored the oxide content of the bath by sampling periodically and analyzing by the LECO method.

3. Alumina feed material: We initially used standard Hall cell alumina for the feedstock. In later runs we switched to a high purity alumina which has a very high surface area and higher content of gamma alumina which dissolves more rapidly in fluoride melts.

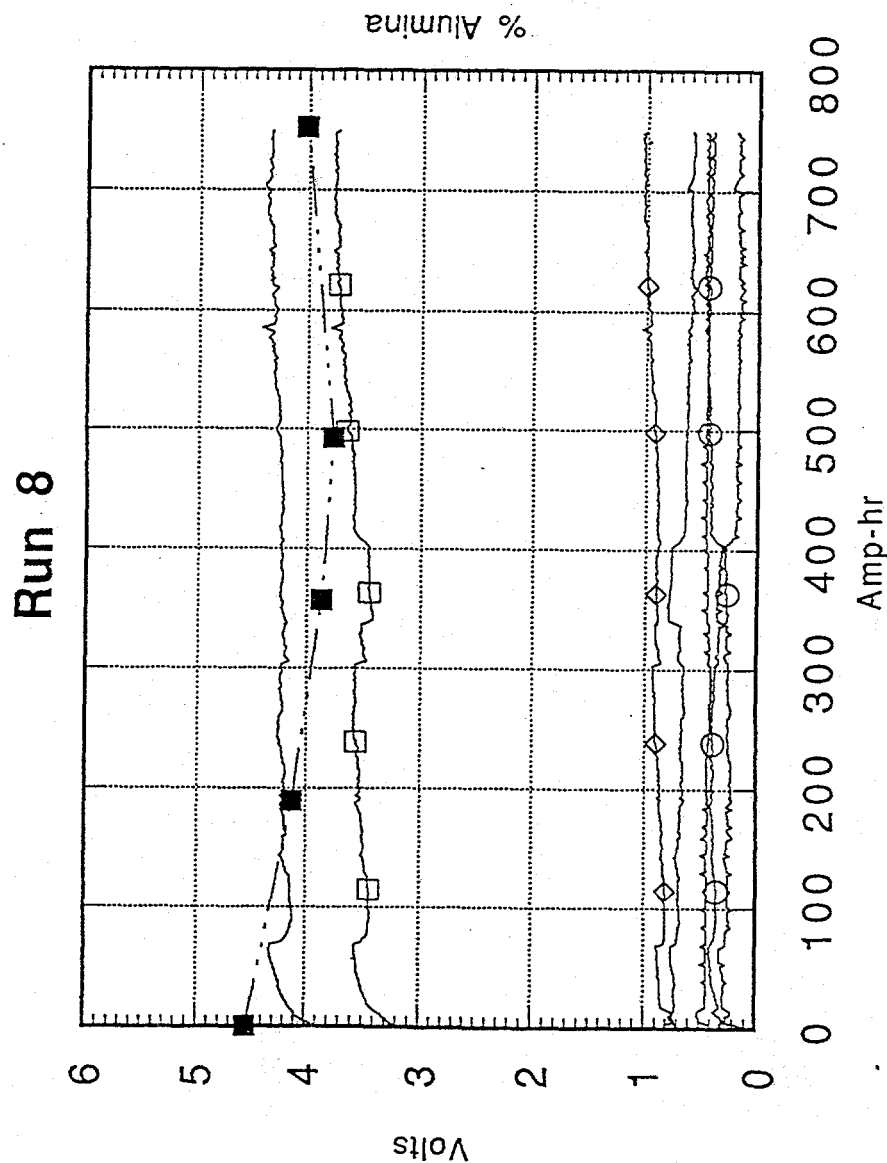
Despite these efforts, saturation was not always maintained. Figure 11 is a typical example from Run #8. It shows that there is a dip in the alumina concentration below saturation which occurs roughly 50 to 200 amp-hours (7-30 hours) after the start of electrolysis. Figure 12 is from Run 30. In the later runs, we tried to overcompensate for this by increasing the feed rate of alumina. However, when we did this; sometimes alumina deposits were created on top of the metal pad. We believe these deposits created other problems. They disrupt the current distribution from the anode and may have locally increased the current density on the anode (potentially increasing the corrosion rate). Figure 13 illustrates this effect on the anode-to-reference ohmic resistance, IR_a . Note that when the deposits were manually broken up, the IR_a immediately decreased indicating that a larger area of the anode was again participating in the electrolysis.

In future cells, the issues of feedstock and feed rate must be resolved. Clearly, the rate of dissolution of alumina must be determined as it will influence the maximum allowable current density, anode corrosion rate, and sludging of the cell.

Some anodes from a large group prepared from the same batch and sintered together in a large furnace had highly variable corrosion rates. It was postulated that rapid deterioration of some of the anodes was due to the argon purge creating slightly less oxidizing conditions at the anode surface compared to an oxygen producing anode alone.

Computer Designation

- Volts (total cell, volts)
- *— atoR (anode to reference total, volts)
- ◇— IRa (anode to reference ohmic resistance, volts)
- ETAa (anode overpotential, volts)
- |— ctoR (cathode to reference total, volts)
- |— IRc (cathode to reference ohmic resistance, volts)
- |— ETAc (cathode overpotential, volts)
- % Alumina

**Figure 11**

**Cell Voltage Components and % Alumina
Concentration Versus Amp Hr**

Computer Designation

- Volts (total cell, volts)
- ♦— atoR (anode to reference total, volts)
- ◇— IRa (anode to reference ohmic resistance, volts)
- ETAa (anode overpotential, volts)
- ctoR (cathode to reference total, volts)
- IRc (cathode to reference ohmic resistance, volts)
- ETAc (cathode overpotential, volts)
- % Alumina

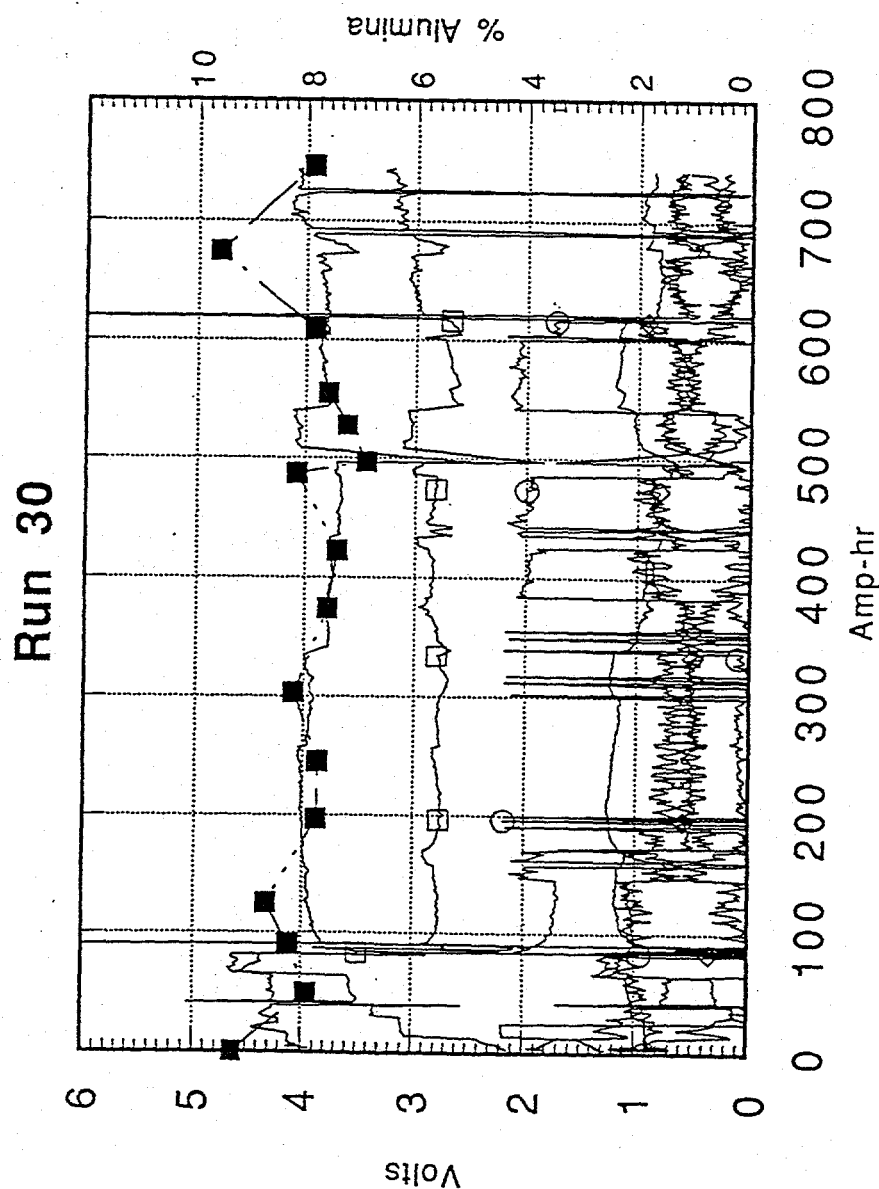


Figure 12
**Cell Voltage Components and % Alumina
Concentration Versus Amp Hr**

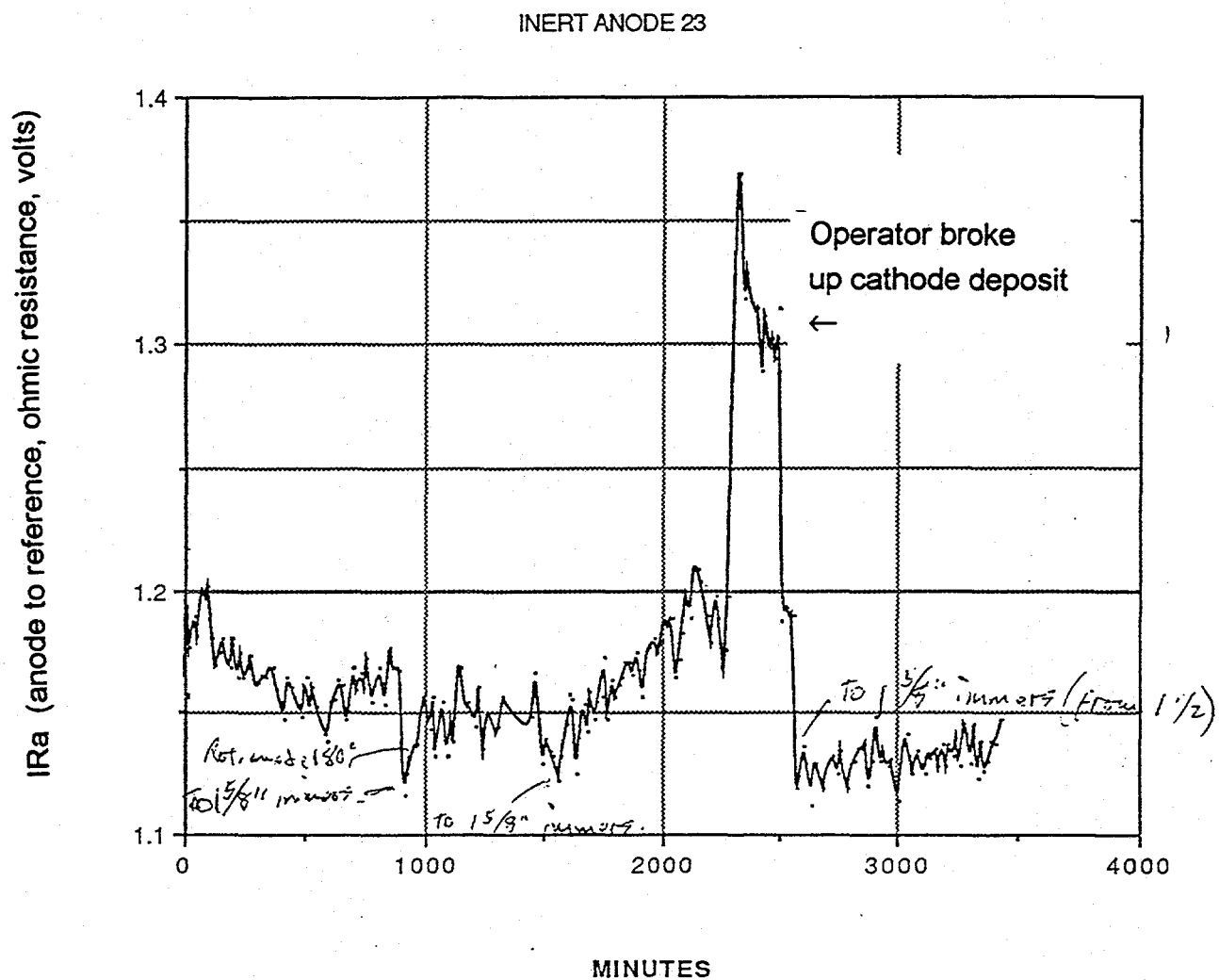


Figure 13

Anode to Reference Ohmic Drop Versus Time

A cell was purged with 100% oxygen instead of argon. Purging with 100% O₂ caused the anode to build up a highly resistive oxide film and the run had to be terminated early. Subsequently, an anode was tested for 100 amp-hours in which the 100% O₂ purge was used for only 10 minutes. The anode was then removed and inspected. The anode was coated with slightly yellowish deposits which were then lightly sanded from surface using 320 grit aluminum oxide paper. The anode then was returned to cell and successfully completed the 100 hour test. Because this procedure worked well, it was established as a preconditioning step without further verification of its effectiveness.

Previous work has indicated that carbon will react with aluminum to create aluminum carbide which is soluble in the electrolyte and is known to accelerate corrosion of the inert anodes by reducing the oxides in the anode. In the present cell design, we have tried to minimize any direct contact of the bath with carbon. Yellow deposits were observed, however, on alumina sleeve and crucible taken from cell. Analysis of scrapings did not indicate the presence of carbides and yellow deposits were most likely iron fluorides.

Anode Corrosion Results

The anode corrosion was determined by analyses of the metal produced during runs and by measurement of the anode diameters before and after the tests. The results are summarized in the Run summary data (Table 6). The metal purity data indicate that significant corrosion was taking place during all tests. The best results were obtained in tests 6, 7, 8, 10, 25B, 26 and 28C. After the tests, the anodes were sectioned as shown in the Figure 14. The bottom section and in some cases other sections were polished and back scattered image and corresponding x-ray images for Fe, Ni, Cu, etc. were taken. Major information was obtained from the bottom section. These images are shown in Figures 15 to 24 for Runs 6, 7, 8, 10, 25B and 28C.

Table 7 shows the distance from the bottom edge where Cu metal can be found. It is seen that in Runs 6, 7, 8, 23, 25B and 28C Cu metal can be found very close to the bottom edge. The best results appear to be the anodes from Runs 6 and 7. But, the anodes in Runs 6 and 7 were cut and polished before mounting, and it is possible that some material may have been lost during this operation - leading to the appearance of a perfect anode bottom for Runs 6

and 7. The analysis of metal produced during the use of anodes 6 and 7 indicate the presence of Fe, Ni and Cu indicating corrosion has occurred.

The analyses for Fe, Ni and Cu in Al during test runs 25B leads to the conclusion that only 0.01 wt% Fe, 0.077 wt% Ni and 0.093 wt% Cu may be attributed to the aluminum produced in this run. However, the loss in diameter of the anode and micro-structural analyses of the anode indicate that the estimated Fe, Ni and Cu concentrations should have been 0.25 wt% Fe, 0.230 wt% Ni and 0.15 wt% Cu.

The apparent anomaly was resolved by analyses of the cathode. A TiB_2 cathode was used during this test. Figures 25 and 26 show the back scattered electron image of the TiB_2 cathode. A layer of Al is found on the cathode and also there is a sludge layer on top of this material which contains Fe, Si, Ni and Cu. Thus the tapped and analyzed metal did not reflect all the impurities that were released from the anode. It is believed that this situation was present only in the case where a TiB_2 cathode was used.

Table 6
Spreadsheet to Calculate Metal Contamination by Inert anode

Run #	Total Amp-hours	Anode Density	Orig. Diameter	Final diameter	Loss in Diameter	Anode Loss (gm)	Anode Loss in/yr	Est. % Fe	Est. % Cu	Est. % Ni
2	800.2	6.55	0.4884	0.4208	0.0676	7.77	2.78	1.08	0.66	1.30
6	460	6.54	0.4715	0.462	0.0095	1.12	0.68	0.27	0.16	0.33
7	749	6.33	0.4771	0.3893	0.0878	9.30	3.85	1.38	0.84	1.66
8	752	6.21	0.4935	0.4752	0.0183	2.13	0.80	0.31	0.19	0.38
10	765	6.22	0.4941	0.4781	0.016	1.87	0.69	0.27	0.16	0.33
15	752	6.29	0.4844	0.4585	0.0259	2.97	1.13	0.44	0.27	0.53
17	754	5.937	0.4912	0.4141	0.0771	8.00	3.36	1.18	0.72	1.42
23	533	6.515	0.4815	0.4597	0.0218	2.58	0.95	0.54	0.33	0.65
24B	773	6.534	0.4838	0.4461	0.0377	4.42	1.60	0.64	0.39	0.77
25B	753	6.542	0.4806	0.4664	0.0142	1.70	0.62	0.25	0.15	0.30
26B	671	6.505	0.4833	0.459	0.0243	2.88	1.19	0.48	0.29	0.57
27C	787	6.523	0.4782	0.4541	0.0241	2.83	1.01	0.40	0.24	0.48
28C	663	6.535	0.481	0.4653	0.0157	1.87	0.78	0.31	0.19	0.38
29	441	6.526	0.4812	0.4657	0.0155	1.85	1.16	0.47	0.28	0.56
30	745	6.536	0.4806	0.3297	0.1509	15.43	6.65	2.30	1.40	2.77

Run #	Total Amp-hours	Metal Heel	Starting			Ending			Est. Metal Conc.		
			% Fe	% Cu	% Ni	% Fe	% Cu	% Ni	Est. % Fe	Est. % Cu	Est. % Ni
2	800.2	582	0.140	0.008	0.006	0.200	0.044	0.080	0.752	0.298	0.592
6	460	2035	0.280	0.010	0.020	0.110	0.010	0.040	-3.332	0.012	0.453
7	749	2035							0.000	0.000	0.000
8	752	641	0.120	0.006	0.002	0.140	0.049	0.042	0.393	0.368	0.336
10	765	540				0.130	0.088	0.067	0.952	0.645	0.491
15	752	540	0.180	0.042	0.040	0.300	0.110	0.140	1.216	0.575	0.805
17	754	600							0.000	0.000	0.000
23	533	600							0.000	0.000	0.000
24B	773	600							0.000	0.000	0.000
25B	753	450	0.140	0.007	0.002	0.100	0.017	0.016	0.010	0.077	0.093
26B	671	450	0.180	0.037	0.049	0.150	0.028	0.037	0.118	0.007	0.009
27C	787	450	0.013	0.001	0.001	0.084	0.055	0.056	0.486	0.352	0.358
28C	663	450	0.15	0.98	0.105	0.11	0.08	0.08	-0.009	-3.941	-0.004
29	441	450							0.000	0.000	0.000
30	745	450	0.14	0.004	0.003	1.96	0.31	0.67	11.866	1.958	4.258

Note: This analysis assumes that all the anode is lost from the diameter. Losses from the bottom are assumed to be small. Metal production is assumed to be theoretical at 75% C.E. 0.25177 gm/A-hour

Table 7

Distance from the Bottom Edge Where Cu Metal is Found

<u>Run No.</u>	<u>Distance (microns)</u>
6	<5*
7	<5*
8	30
10	<20
23	30
25B	30
26	20
27B	40
27C	<20
28C	<20
29	40

Inert Anode S#579589-9

100 Hrs.

800 C

765.15 Amp Hrs.

7.52 Amps

4.3 - 4.4 Cell Volts

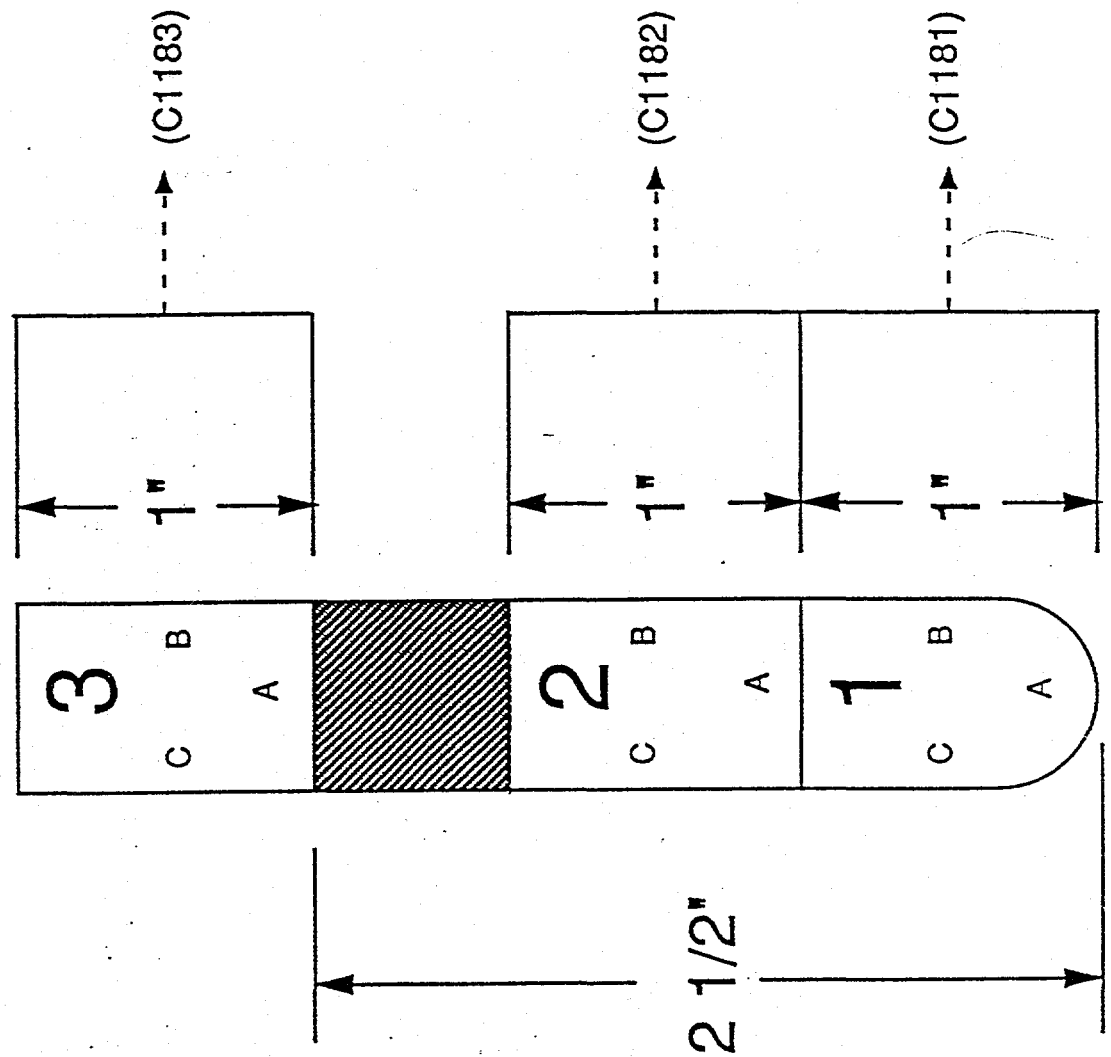


Figure 14

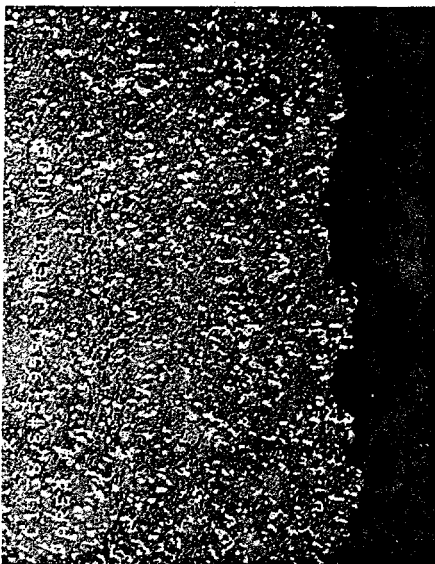
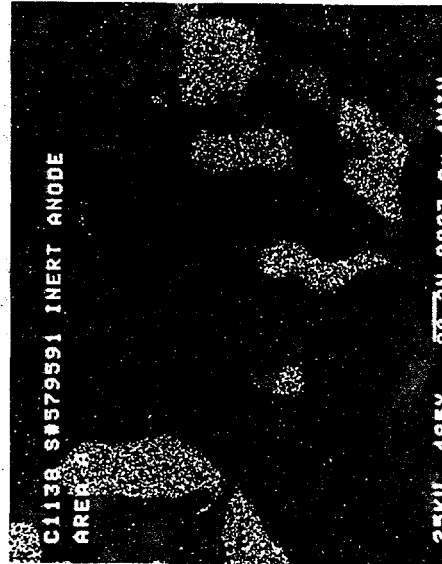
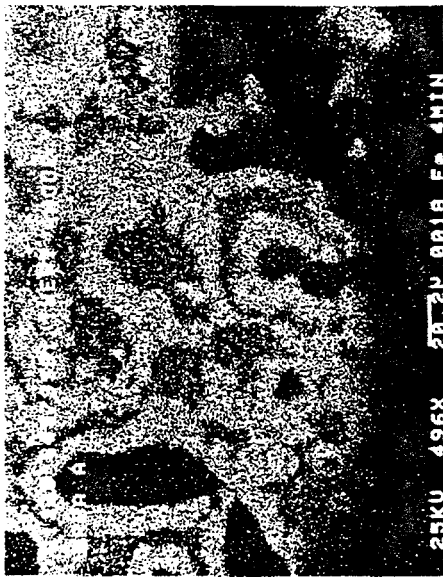


Figure 15 Run 6, Section 1A

GA 31331.1

S# 579587
36% NaF
64% AlF_3
764.6 amp hours
3/4 amp/cm²
800°C 1 1/2" depth

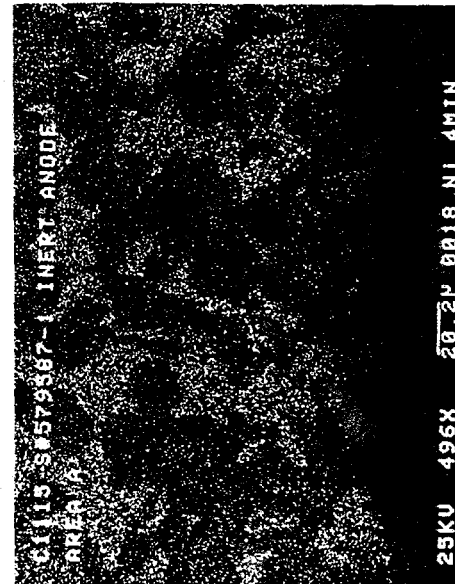
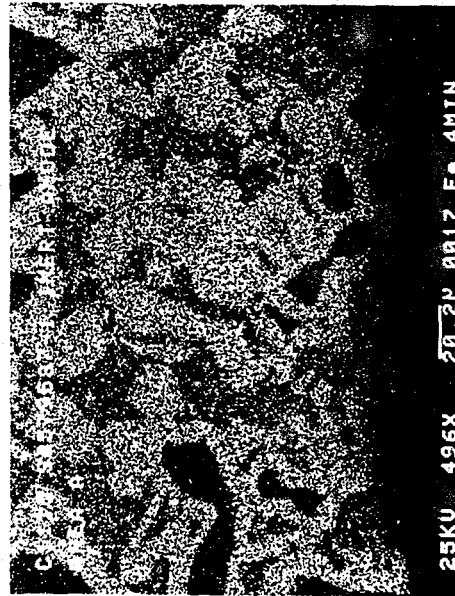
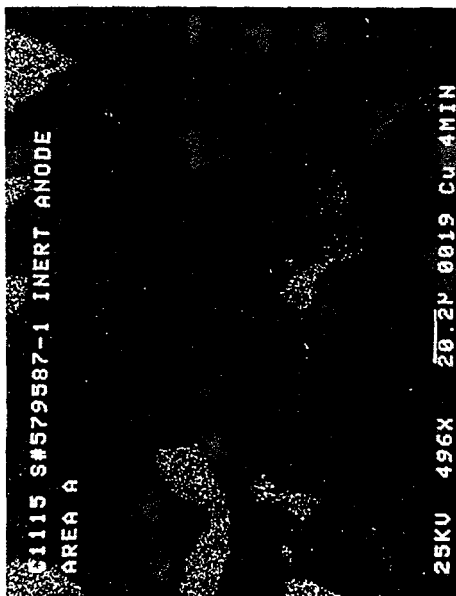
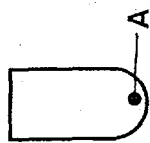


Figure 16 Run 7, Section 1A

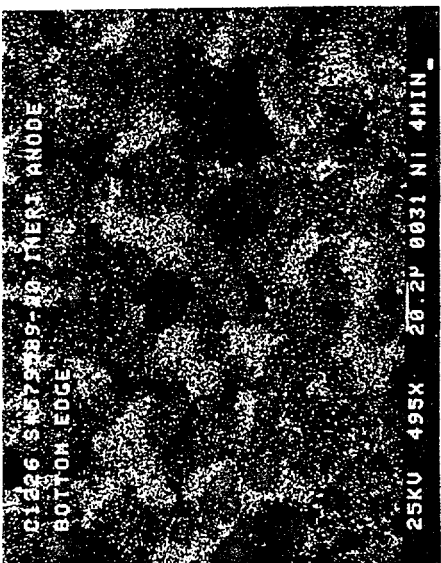
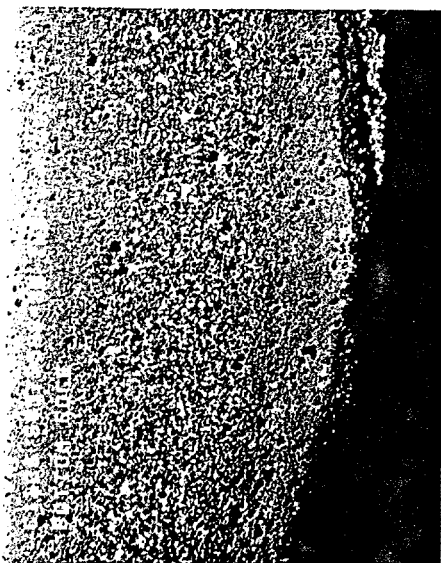
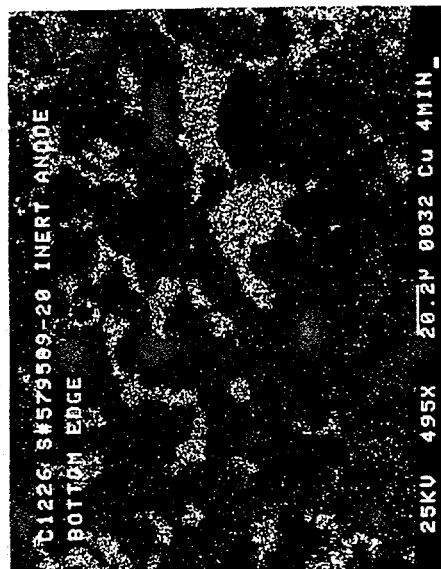
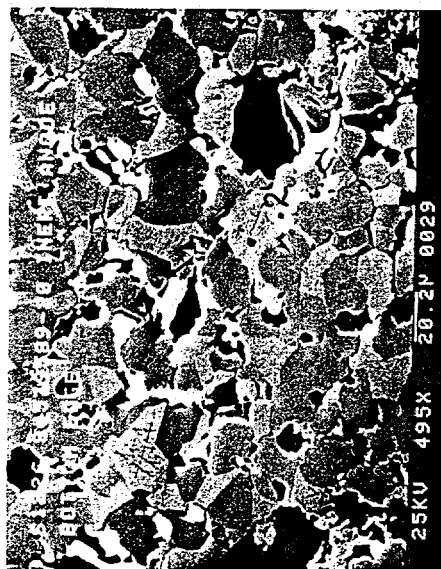
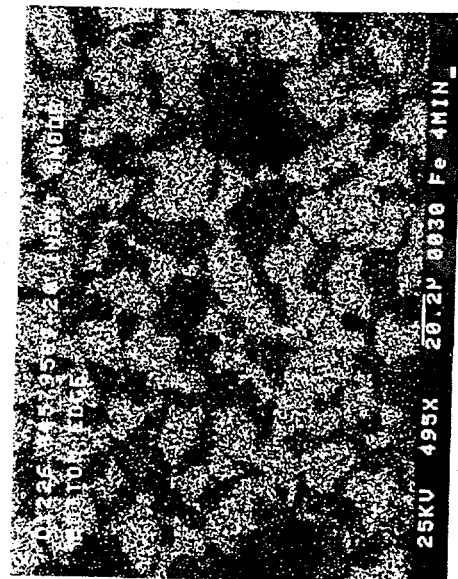


Figure 17 Run 8, Section 1A

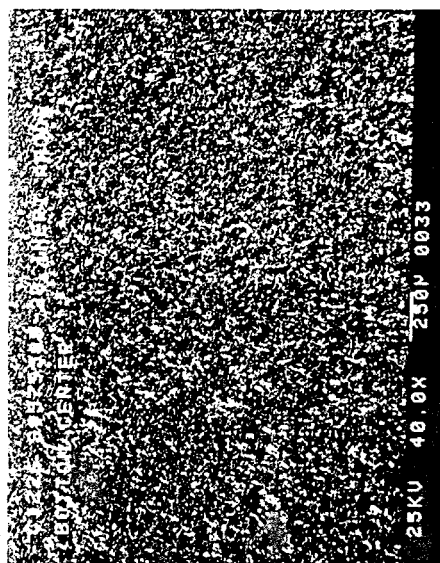
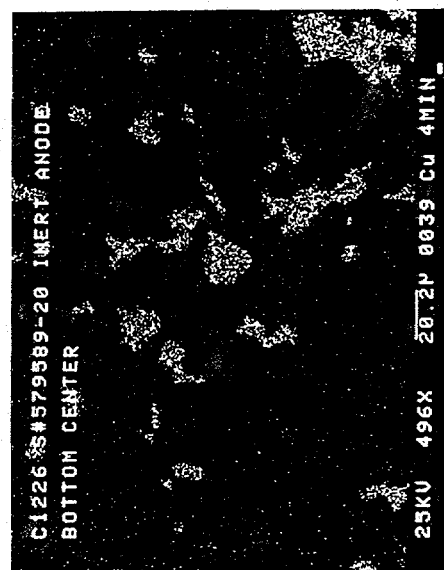
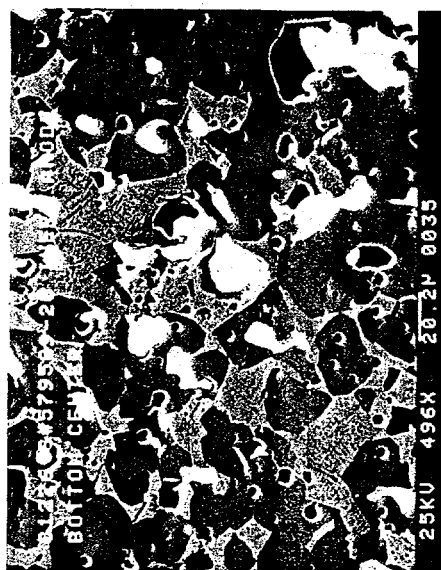
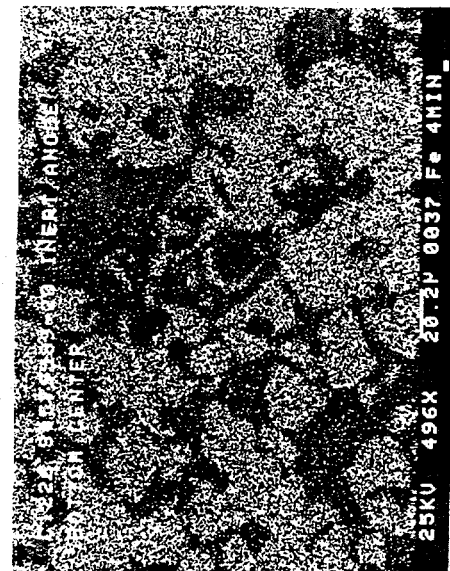


Figure 18 Run 8, Section 1B

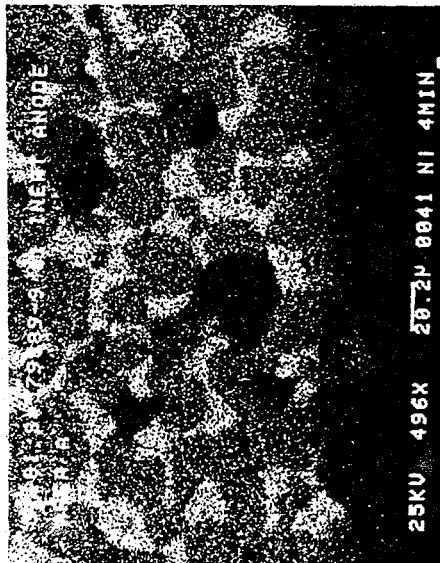
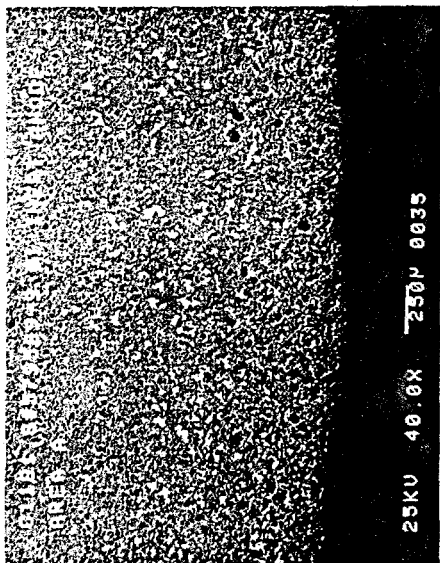
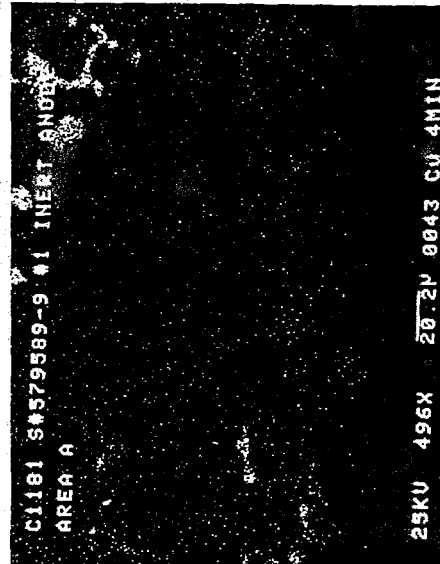
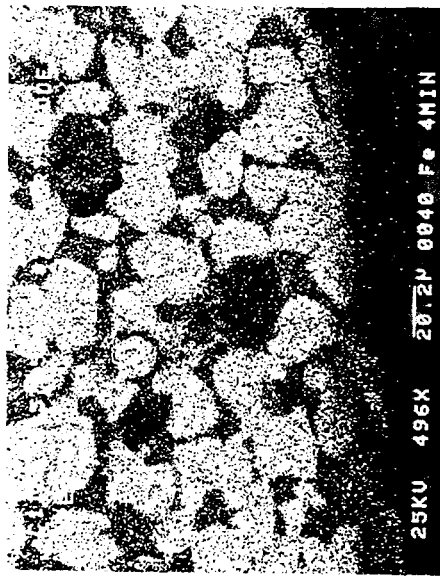


Figure 19 Run 10, Section 1A

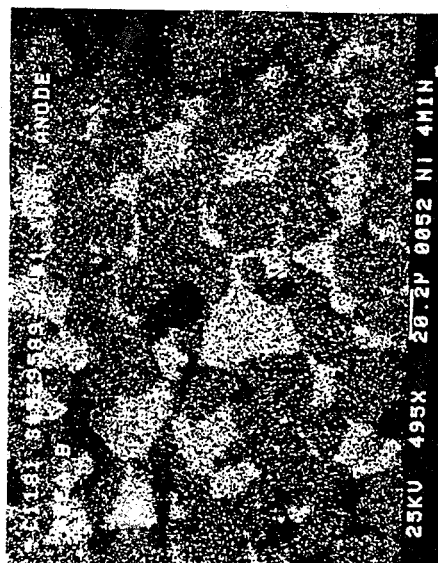
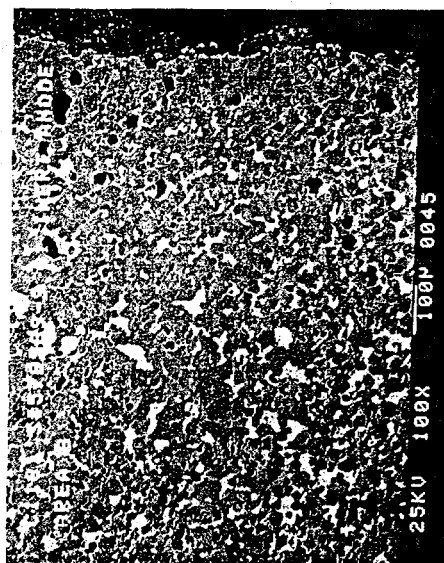
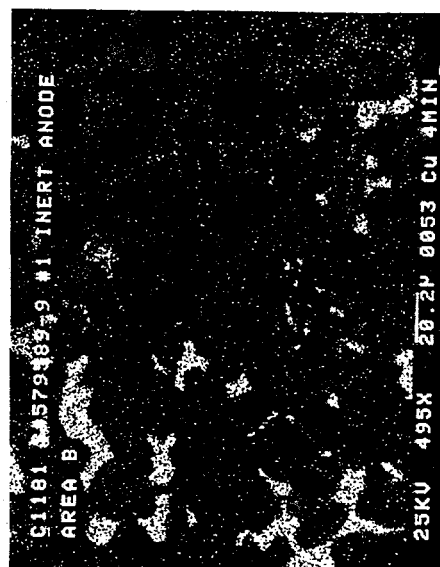
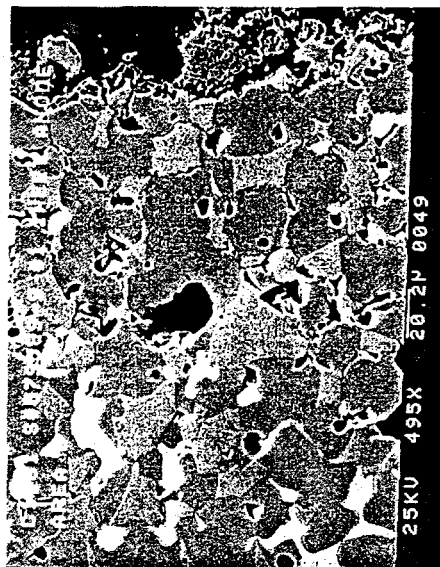
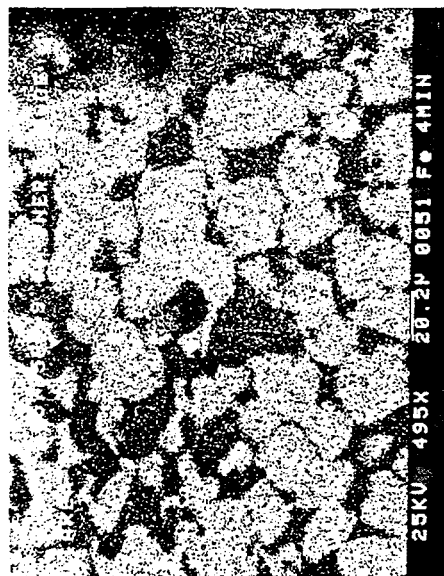


Figure 20 Run 10, Section 1B

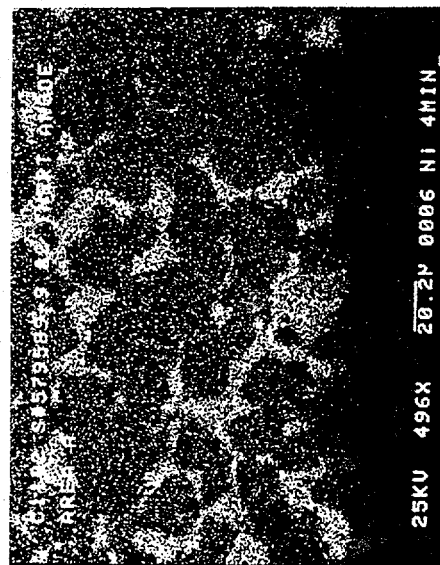
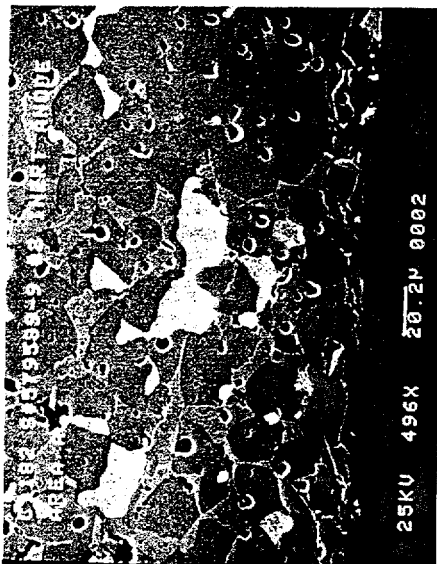
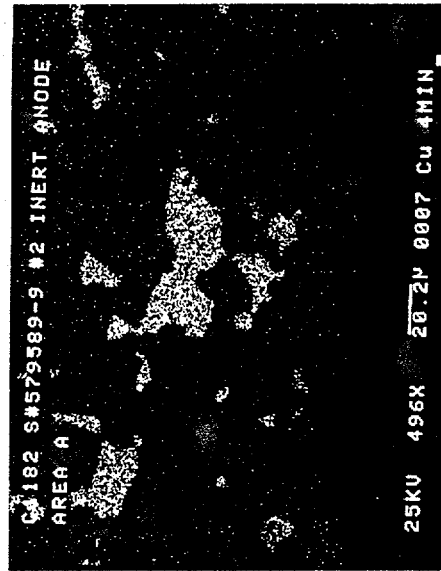
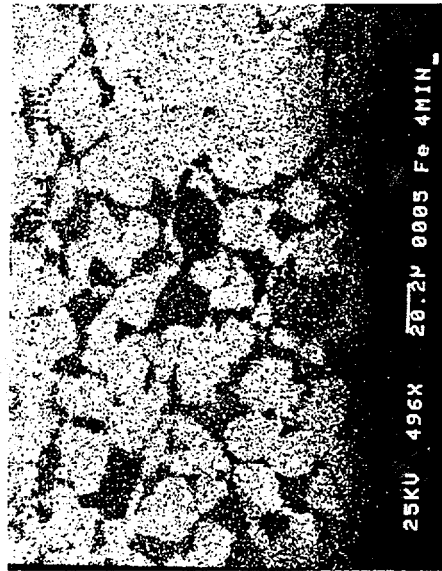


Figure 21 Run 10, Section 2A

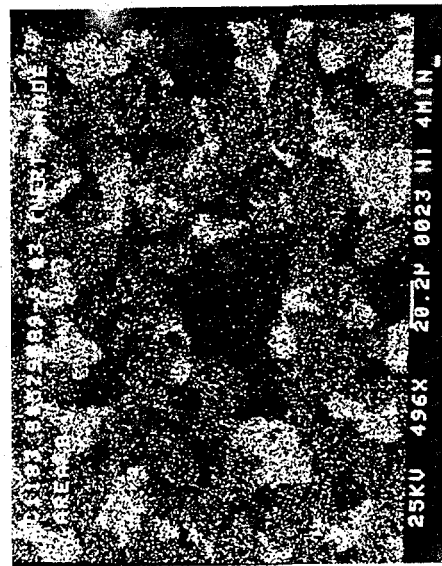
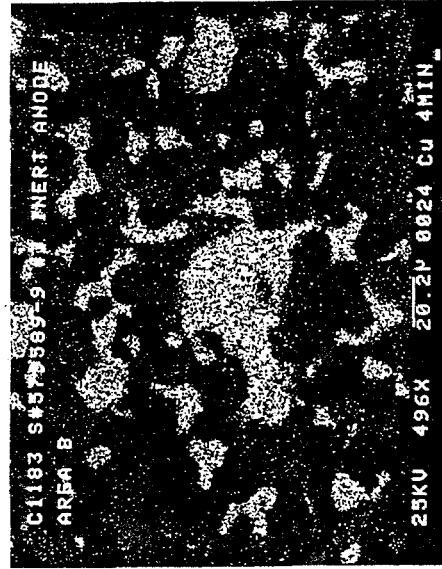
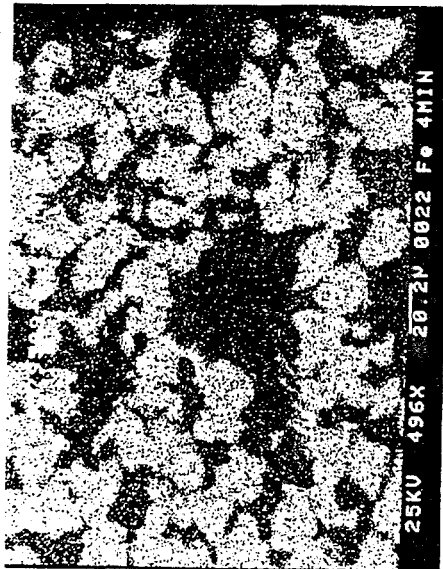


Figure 22 Run 10, Section 3B

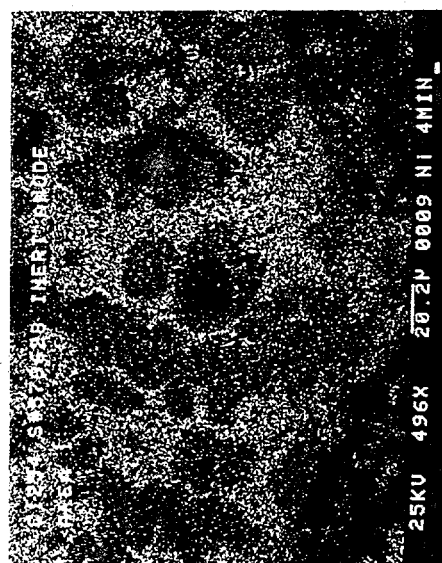
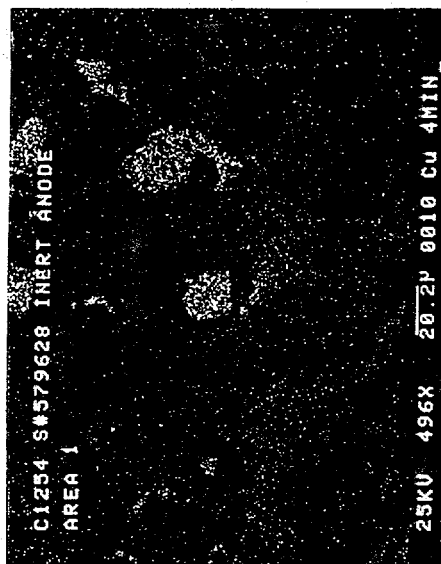
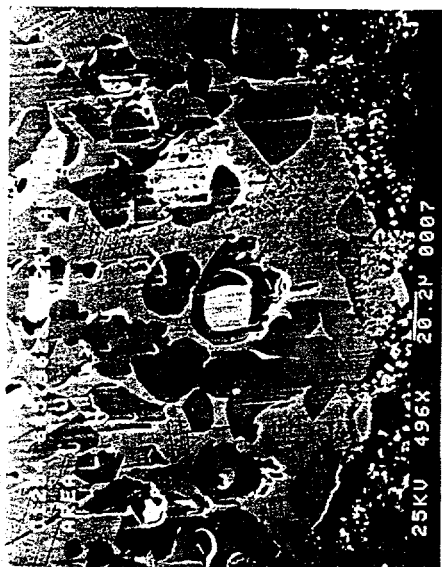
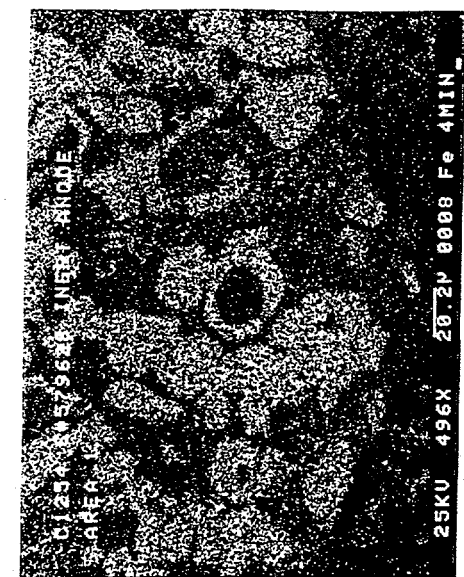


Figure 23 Run 25B, Section 1A

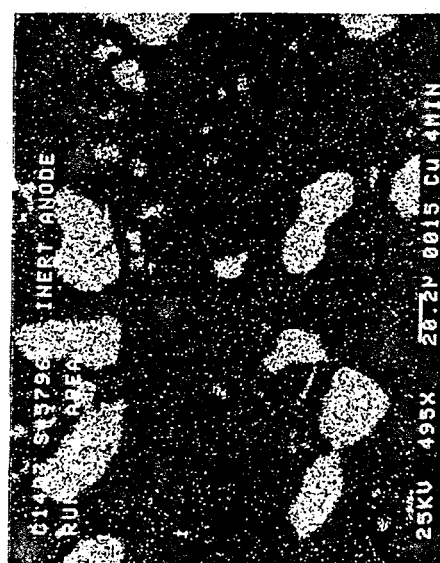
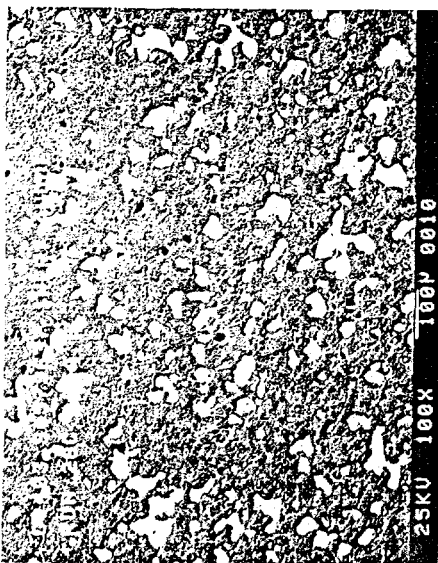
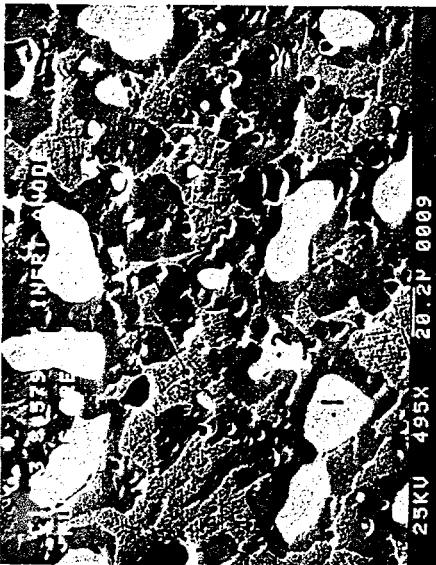
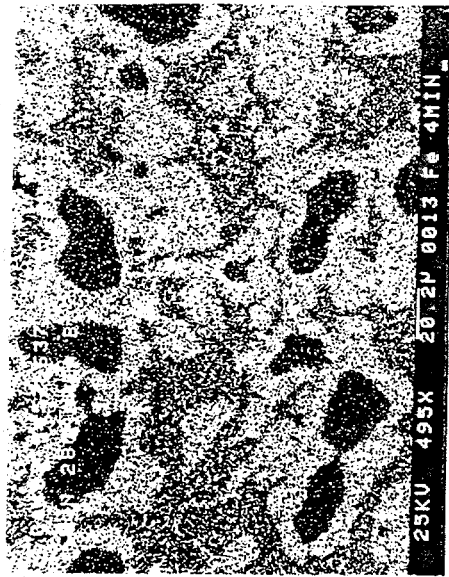


Figure 24 Run 28C, Section 1B

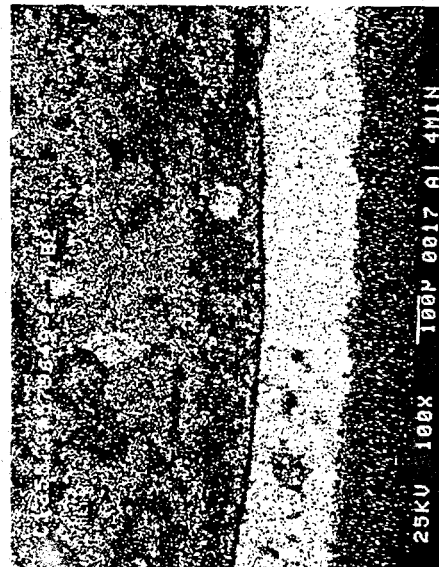
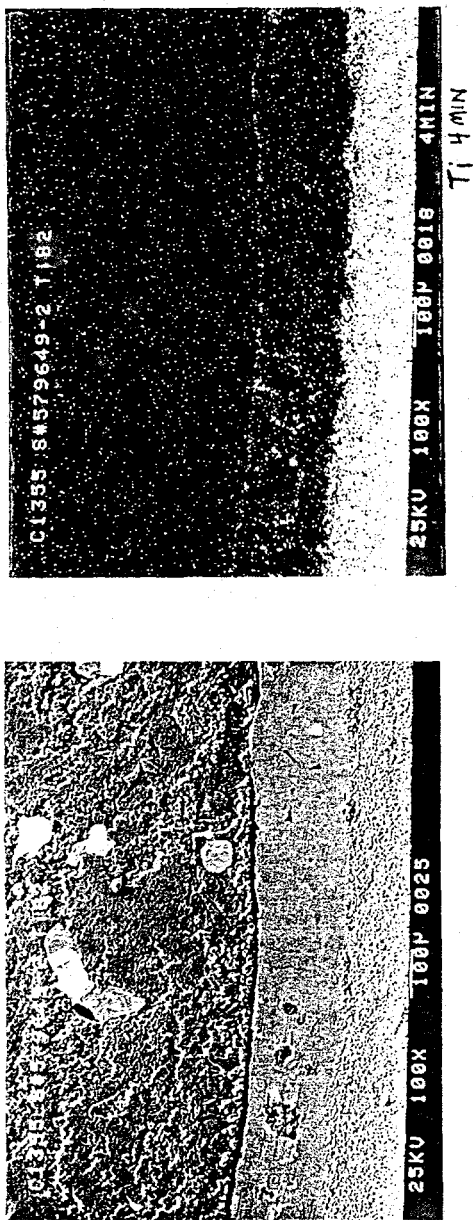


Figure 25 Runs 25 and 26, Cathode

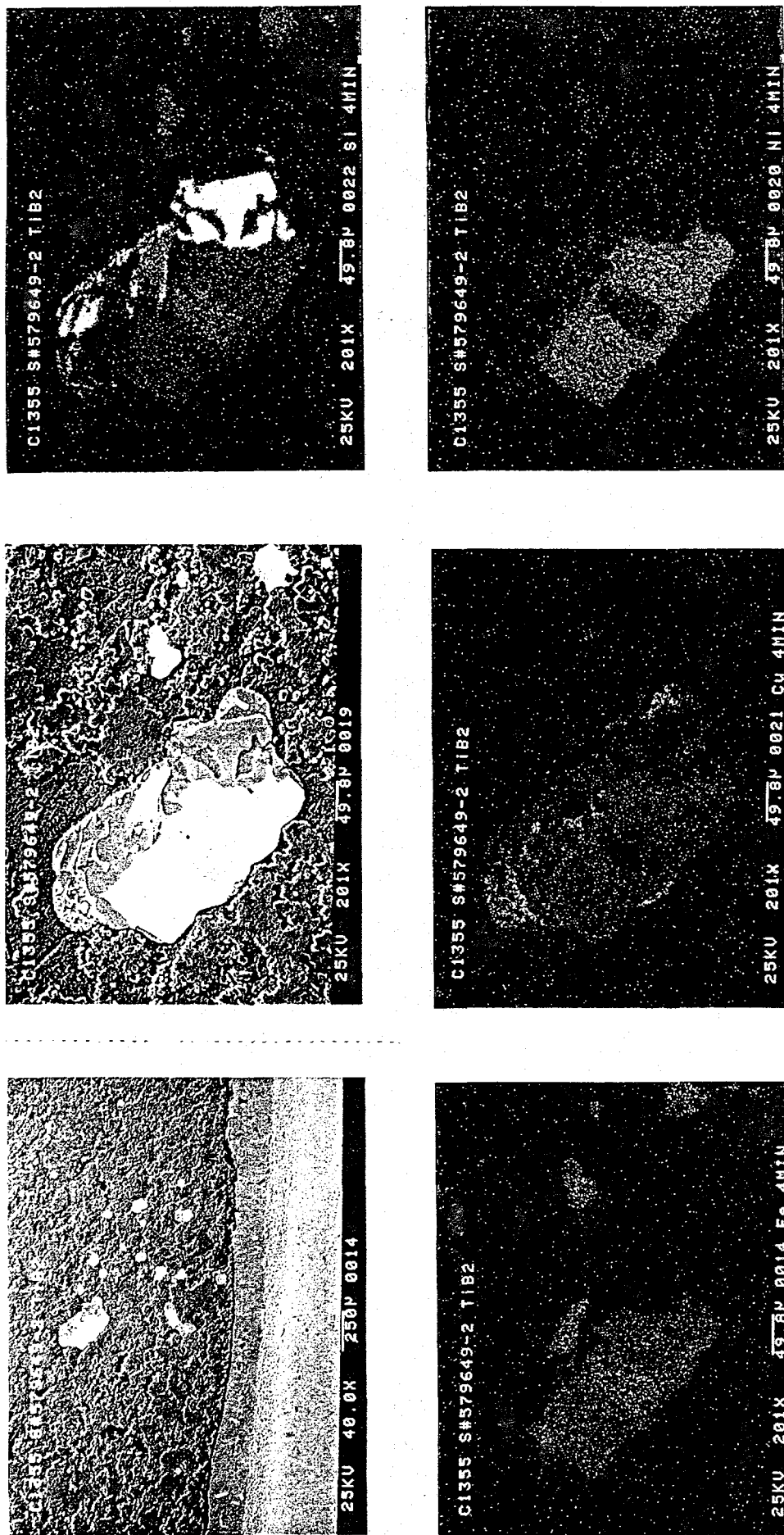


Figure 26 Run 25 Sludge Near TiB₂ Cathode

OBJECTIVE FOR 200 HOUR RUNS

The overall objective of this research is to assess the commercial viability of using high surface area anodes and a low temperature electrolyte in aluminum reduction cells. This section of the report describes the work designed to achieve two 200 hour anode corrosion tests. Successful operation is targeted to occur in two of the three 200 hour experiments, and anode corrosion rate and metal purity will be quantified as a function of time. Closing the mass balance; that is, determining the final location of anode constituents will be attempted.

RESULTS: SUMMARY OF LOW TEMPERATURE DOE RUNS DESIGNED TO ACHIEVE 200 HOURS

BENCH CELL RUN 200-3

Six anodes were tested simultaneously in 6 different cells. These tests provided direct comparisons on feed type, bath composition and cathode current density to select operating parameters for the first attempt at a 200 hour run - which was done in Run 4. The key comparisons were as follows: 1) MGA - standard metal grade alumina used to feed conventional smelting cells was compared with FAH - flash activated hydrate which has a higher water content to promote dissolution in the electrolyte. 2) Electrolytes with and without 10 % CaF_2 and electrolytes with ratios of 0.5 and 0.56 were compared. 3) Cathode current densities of 0.1 and 0.3 amp/cm^2 were compared because larger area cathodes (lower current densities) are a larger source of soluble aluminum.

The main findings were: 1) No significant difference in anode film resistance or anode corrosion was demonstrated from using FAH feed versus using MGA feed in this short test (~24 hours). 2) The high calcium electrolyte resulted in the highest anode corrosion, and this could be due to the higher density of this electrolyte causing some flotation of aluminum droplets. The lower ratio electrolyte test also showed higher anode corrosion. 3) No difference in anode corrosion due to cathode size was proven from these short tests.

Based on these results; MGA was selected as the feed, CaF_2 was not added to the electrolyte, the cryolite ratio was maintained at 0.56, and the cathode was not reduced in area for Run 4. The cell design was changed from previous work to enhance circulation as shown in Figure 27. The bubbler was not surrounded by alumina balls as it was for the 100 hour runs. It is

believed that increasing circulation will promote Al_2O_3 saturation in the electrolyte and reduce concentration gradients at the surface of the anode. The design also avoided any possible contact with carbon which has been implicated in some tests as an anode reductant.

BENCH CELL RUN 200-4

This was the first attempt at a 200 hour, low temperature cell test. The low temperature cell operated 177 hours without a significant anode voltage transient till near the end of the run. The anode resistance began increasing only about 10 hours prior to the shut down. Run 4 is believed to be the longest, best controlled test that has been run at low temperature (800°C). The cell was overfed a factor of 2 and circulation of bath and entrained alumina appeared high based on high LECO values between 5% and 10% with a few results much higher (21%) compared to a 4.2% saturation level for alumina at 800°C . Figure 28 shows cell voltage components versus time over the test period.

The wear pattern was low near the bottom of the Cermet anode (<0.6 inches per year) but increased to a maximum above the bath argon interface of about 2.0 inches per year. One theory would attribute this pattern to water content of the feed producing HF by reaction with the electrolyte while another theory concluded that the circulation pattern could direct aluminum toward the top of the anode. The high amount of entrained alumina determined by LECO analyses does indicate the potential for metal circulation especially with the smaller density differences between bath and metal expected at lower temperature operation. The failure of cathode protection sleeves could have provided aluminum droplets to the circulating bath. There is even the possibility of alumina particles entrained in the circulating electrolyte increasing wear of the anode.

Run #4 - 200 Hrs
Run #5 - 200 Hrs

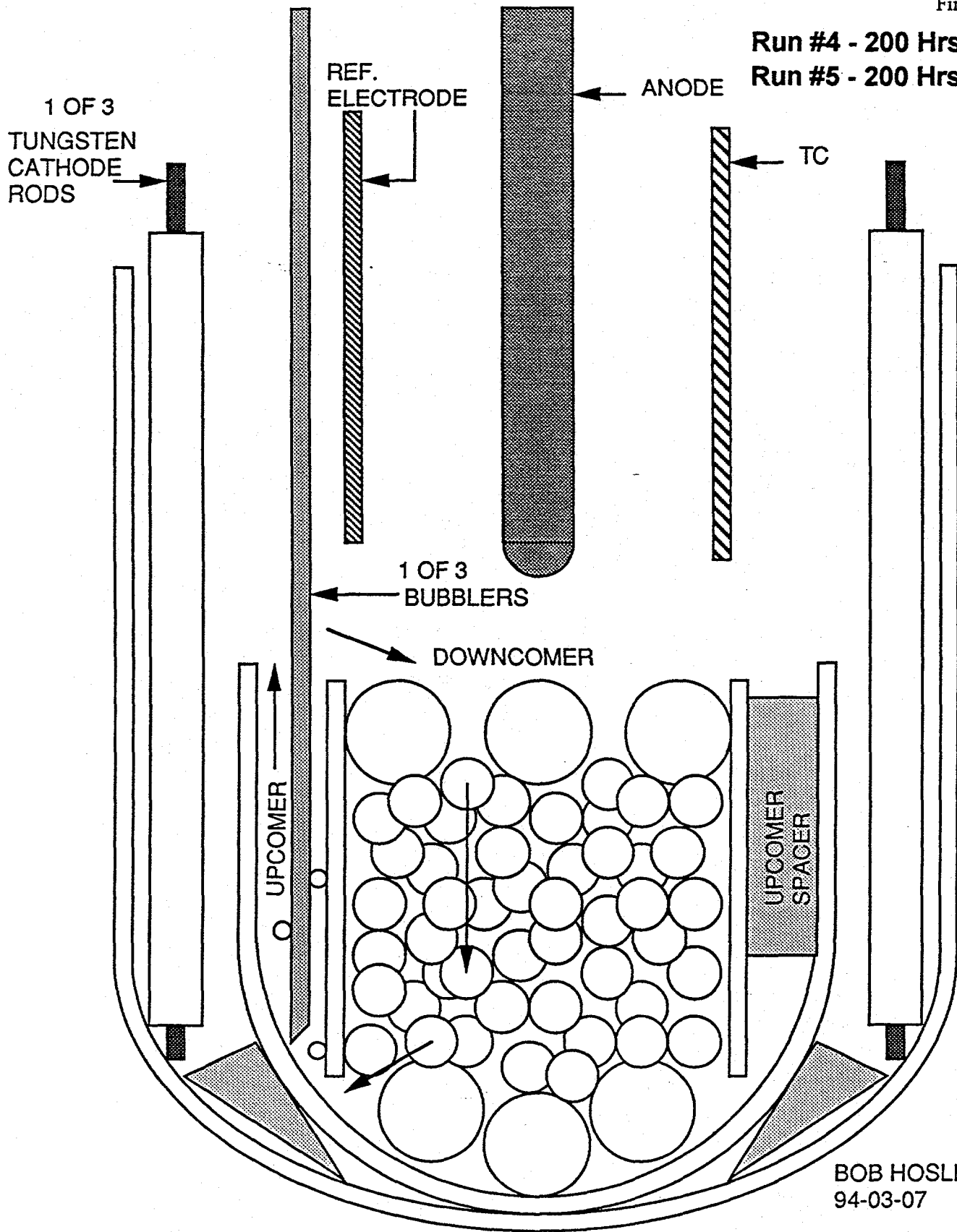
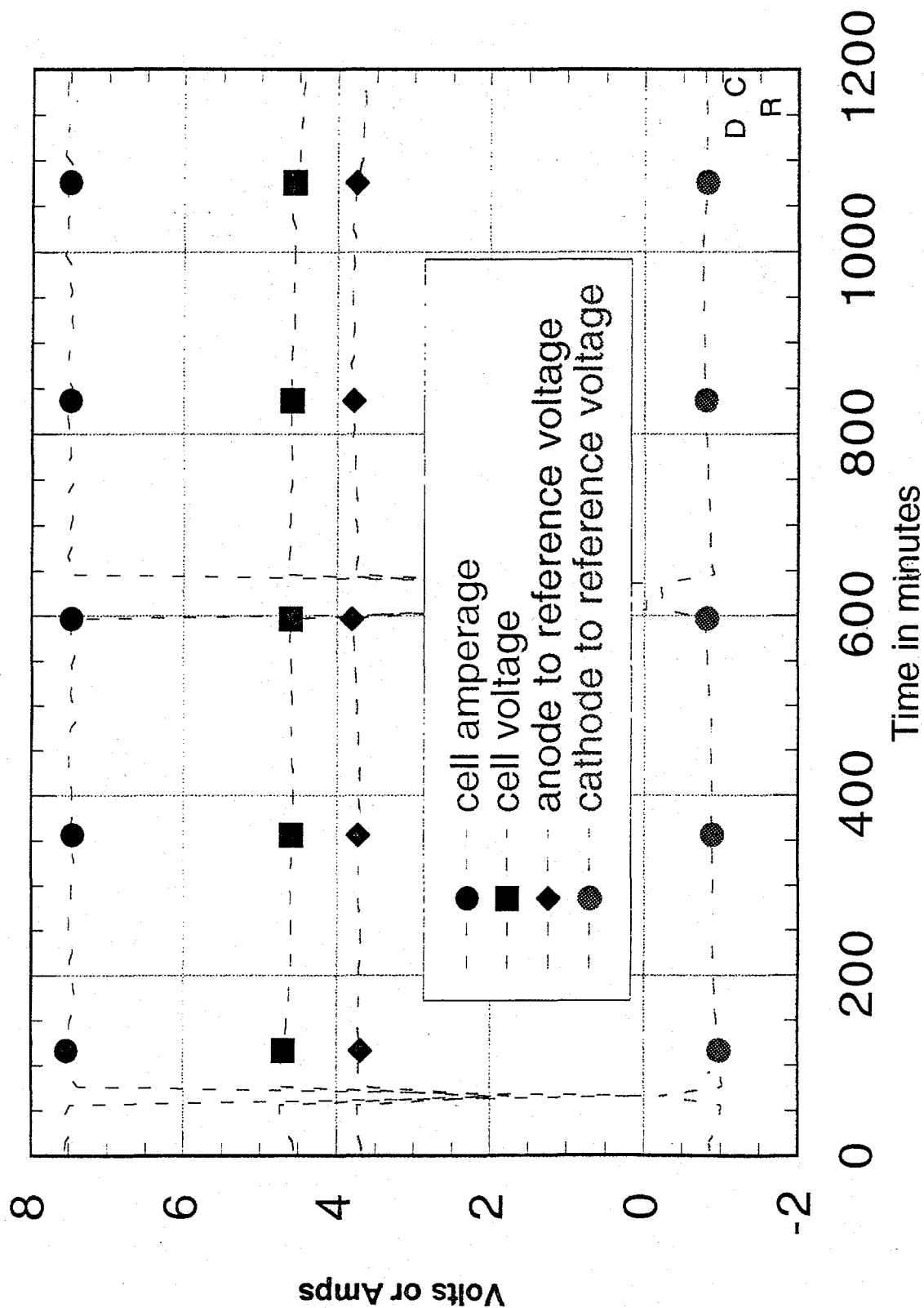


Figure 27. Cell Design, Run 4-200, Run 5-200

Figure 28.

Cell Parameters 4th Run



BENCH CELL RUN 200-5

This was the second attempt at a 200 hour test and operational changes were made to reduce anode corrosion as follows:

- 1) Anode exposure to HF (which is produced from moisture in the alumina feed reacting with the electrolyte) was reduced in hopes of eliminating this possible mechanism of anode wear. One method was to pre-feed the cell with excess alumina before installation of the anode while the other method preheated all feed to 600°C just below the lid of the cell.
- 2) An oxygen purge was used in hopes of offsetting the smaller than typical anode to cathode ratio of the bench scale cell. There is concern that the oversized aluminum cathode area (relative to the anode area) provides excessive soluble aluminum which could cause higher anode corrosion than a more correct ratio between anode and cathode. The extra oxygen would simulate a larger anode area and react with some excess soluble aluminum. O₂ was used in the 100 hour runs to precondition. For this 200 hour run trial, the O₂ was diluted with argon and the circulation was expected to be higher.
- 3) A reduction in cathode deposits was sought. The electrolyte was premelted in a separate crucible and insolubles were given time to settle to the bottom of the crucible. This region was separated from the solid electrolyte which was later charged to the cell. It is believed that this material contributes to cathode deposits.

The design of this cell was similar to the Run 4 unit (including the circulation pattern) as shown in Figure 27.

Even though the bath constituents were premelted and the bottom sludge layer removed, high resistance at the cathode did occur at start up, but was reduced with bath ratio corrections. This ratio change was initially blamed on fume losses during the bath premelting procedure. It was later found to be difficult to obtain and sustain ratios below 0.6 at startup.

Several Cermet anodes were used in attempts to provide a 2nd 200 hour run at 800°C. All of these anodes developed high resistance at the anode within several hours of operation. It was

found possible to operate these anodes at reduced current densities, but the use of oxygen purges tended to increase the anode resistance and had limited use. The major problem was difficulty in achieving dissolved alumina values over 3.5 %. LECO values during operation were as high as 9% because of undissolved entrained alumina. When the bubbler induced circulation was shut off and the undissolved alumina settled, values as low as 2.7% were obtained within a few hours indicating the difference was circulating undissolved alumina .

The difference between these tests and the first 177 hour run was the reduction of the amount of water entering the cell in the feed and time for the feed to mineralize to alpha alumina. The dry alumina was extremely difficult to dissolve. It is postulated that conversion of this feed to alpha alumina in the low ratio bath or the fume was probably a factor in not achieving saturation of the electrolyte.

A higher level of dissolved alumina was achieved for most of Run 4 (the 177 hour run) and the higher water content of the feed and mineralization of the feed in Run 5 are the apparent reasons.

Anodes were operated from 24 up to 100 hours during these tests, with the last anode lasting for 100 hours but experiencing catastrophic wear during the last 48 hours because of the aforementioned alumina dissolution problem. Circulation of aluminum droplets was also a factor in anode corrosion. Tungsten cathode rods swelled after prolonged contact with molten aluminum and broke the alumina protection tubes; and this may have enhanced the availability of circulating aluminum and corrosion of the anode.

After Run 5 several corrosion tests without electrolysis were done before shutdown and autopsy of the cell. Two of these tests showed surprisingly high wear rates of 0.7 in/year and 1.5 inch /year even though there was no electrolysis, and this supports the idea that metal circulation and cathode failure was a factor during these runs.

A new unit was designed for Run 6 to change the flow direction away from the anode. The flow direction was reversed by switching "upcomer" and "downcomer" compared to the cell design used in Run 4 and Run 5. The "upcomer" and bubblers are near the center of cell while the "downcomer" and filter balls are between the cathode and "upcomer" as shown in Figure 29. The circulation pattern is opposite to the direction of migration of aluminum from the cathode. Prior to the Run 6 electrolysis test, this new unit was also used for additional

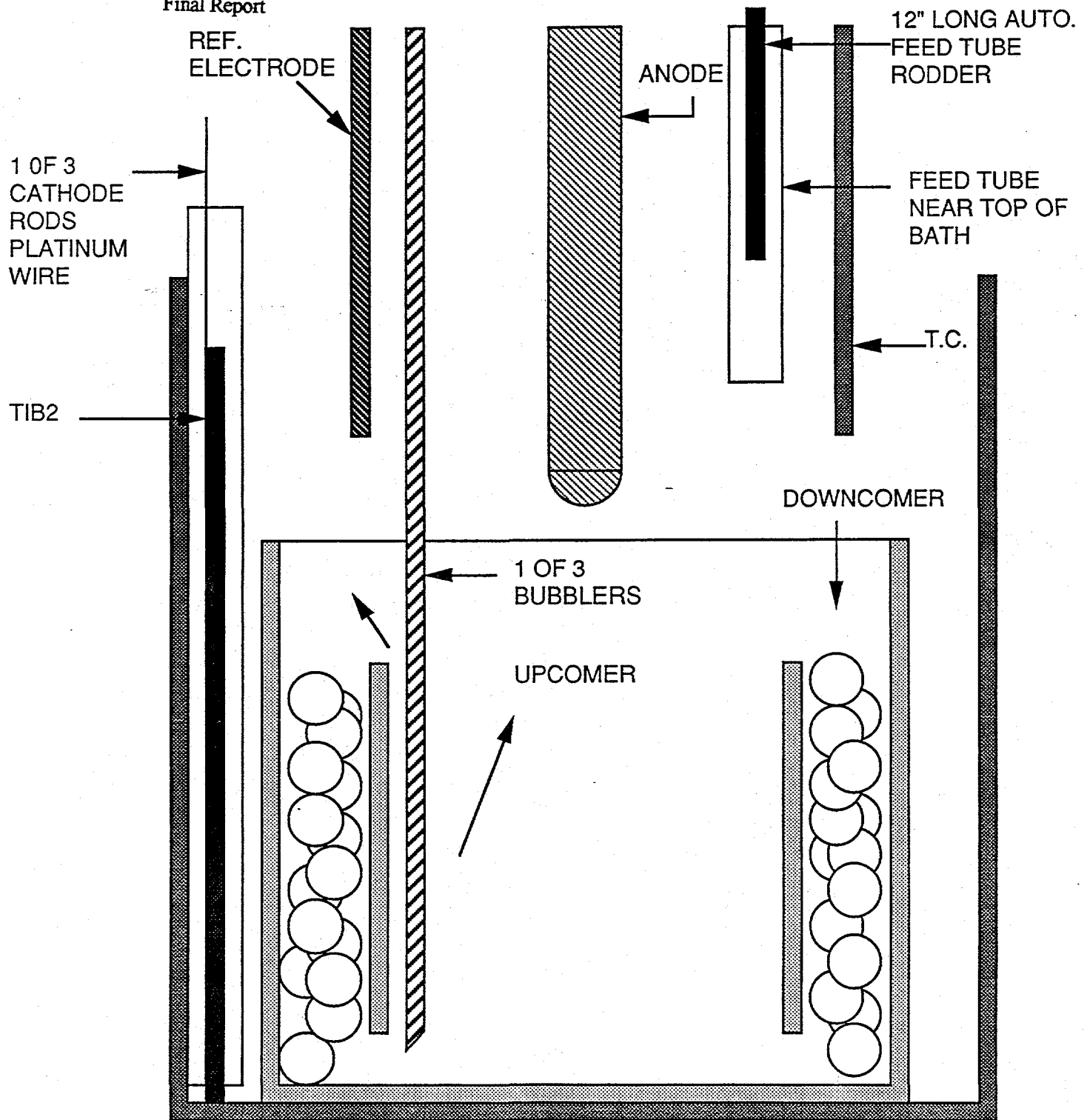
corrosion tests without electrolysis to provide some comparison with the Run 5 tests. These non-electrolysis tests all showed much lower wear rates (0.09 inch/year to 0.27 inch/year) than the Run 5 non-electrolysis tests.

BENCH CELL RUN 200-6

This was the third attempt at a 200 hour test with operational and design changes as follows:

1) Flash Activated Hydrate (FAH) feed with high water content was used to enhance dissolution in the low temperature electrolyte while Run 5 had used pre-heated alumina and had very rapid increases in anode resistance which are attributed to low alumina in the electrolyte. 2) The flow direction was reversed by switching "upcome" and "downcomer" compared to the Run 4 and Run 5 cell designs as previously discussed. 3) The tungsten cathode rods were replaced with sleeved, graphite rods immersed in the metal pad. In previous runs, tungsten cathode rods swelled after prolonged contact with molten aluminum and broke the alumina protection tubes; and this may have enhanced the availability of circulating aluminum.

After melting of the electrolyte, the bath ratio (NaF/AlF_3) was much higher (over 0.7) than expected which was also the case in the previous run. In this case, ratio corrections (NaF additions) were made before start up of the cell, and high cathode overvoltages were reduced at start up. The ratio was only corrected to about 0.62 rather than 0.56 because it seemed increasingly difficult to dissolve alumina (even the FAH with the high water content) at the lower ratios. Early cell operation for Run 6 was improved using feed with high water content compared with Run 5. No problems with high anode resistance were encountered with the Run 6 anode until the alumina content dropped below 3.2 % due to an accidental loss of feed to the system. The resulting high anode resistance could not be eliminated even at reduced current density. The anode was removed from the bath but kept in the fume above the bath, and this may have contributed to the inability to eliminate high anode resistance. The anode corrosion was found to be unacceptable and unusual; in that, there were deep pits instead of even wear. Autopsy revealed that the graphite rods used as cathode connectors had become tapered and carbon had probably entered the electrolyte and could have reacted with the anode.



RUN 6, 7, 8, 9 D.O.E. LOW & HI TEMP.

**BOB HOSLER
95-01-16**

Figure 29. Cell Design, Run 6, 7, 8, 9-200

BENCH CELL RUN 200-7

This run was setup to be similar to Run 6 except graphite cathodes were eliminated in favor of the tungsten cathode connectors. Graphite cathode connectors were considered even more of a problem than the tungsten cathodes connectors because of the aforementioned wear problems experienced in Run 6. No solution to the cathode connector problem was implemented. This cell incorporated an automatic shutoff system which allowed operation over long periods without the presence of an operator.

This test showed no indication of any high resistance problems on the anode which was removed from the cell after 105 hours only because of a broken cathode connector rod with plans of continuing the test with the same anode in Run 8. The wear rate measurements on the anode were less variable than Run 4 ranging along the length from 1.14 inch/year to 1.55 inch/year with an average at 1.28 inch/year.

BENCH CELL RUN 200-8

The inert anode with 105 hours from Run 7 was operated for an additional 30 hours for a total of 135 hours before high resistance on the anode and premature crucible failure shut down the cell. This anode had a high resistance before the start of this run. Although resistance was not a problem during Run 7, a resistance measurement after removal did show a high resistance layer after the anode cooled down. This is typical and this resistance layer might be associated with fume exposure during removal, thermal cycling or even a layer of frozen bath. There was also some accidental voltage cycling due to a control system flaw during this run. The wear rate measurements on this anode for this 30 hours were much more variable ranging from 0.57 inch/year to 3.66 inch/year with an average at 2.03 inch/year. Figure 30 shows cell amperage and voltage over time for this test

BENCH CELL RUN 200-9

The high resistance layer remaining from Run 8 was removed by machining until a normal electrical resistance was measured, and this anode was installed in a new cell to increase the hours of DC electrolysis. This cell had a larger round bottom crucible than previous cells.

This run resulted in a total operational time of over 235 hours and this last test indicated minimal corrosion but high anode resistance caused a continual reduction in current density during the test.

The wear rate for this last 98 hour campaign on the same anode was much lower than previous tests at an average of 0.29 inch/year. If one data point is eliminated, this drops to 0.1 inch/year, but the current density had to be reduced continually during the test.. This result is comparable to the non-electrolysis circulation tests with aluminum in the sump done prior to Run 6. The results are much better than the non-electrolysis circulation tests which followed Run 5.

CONCLUSIONS

- Two long corrosion tests were completed operating at low temperature (800°C) compared to typical operating temperatures of about 960°C. The first test lasted 177 hours and had a very uneven anode wear with the bottom of the anode having low wear rate of about 0.6 in/year and the top higher at 2.0 inch/year. It is believed that this pattern was due to circulating metal droplets from the cathode region impinging on the anode. The second long test was done in three steps for a total of 235 hours and it did show a very low wear rate (0.1 to 0.3 inch/year) for the last step of the test. This low wear rate did correspond to an increase in anode resistance which forced current density down and could not be eliminated even at very low current densities ($< 0.1 \text{ amp /cm}^2$). This very low wear rate does support the hypothesis that wear rate could decrease with time. The high resistance and low current density were disappointing, however. The anode surface resistance could have been effected by fume exposure and thermal shock caused by the two changeouts which were required to attain this 2nd long term electrolysis test.
- The cathode connector may have contributed to higher wear rates. No long term solution to the cathode connection problem was implemented for these runs. Failure of the alumina sleeve which protects a tungsten connecting rod can lead to circulating metal droplets (especially in Run 4 and Run 5), and this could be enhanced at lower temperatures because bath and metal densities tend to be closer. This is aggravated by the fact that the preferred low temperature electrolyte ratio of 0.56 was difficult to achieve and sustain for all of these tests. Maintaining a sufficient density differential between the

electrolyte and aluminum cathode is difficult at low temperature. The electrolyte increases in density faster than the metal as the cell temperature is decreased, but lowering the ratio to 0.56 would offset the temperature effect. These runs tended to operate at a higher ratio, however, and this would have enhanced the possibility of metal droplet flotation or circulation. This implies that somewhat higher temperature operation is required to maintain an acceptable density differential between bath and metal.

- The feed alumina seems to be rapidly mineralized to alpha alumina even at low temperatures in these low ratio electrolytes while preheating the feed on the lid may have caused a crystal size change which inhibited dissolution rather than a conversion to alpha alumina. In either case this material is very slow to dissolve under these conditions. It has been necessary to overfeed to maintain saturation and this causes sludge build up and loss of alumina to the process. This is a serious economic problem for low temperature operation. An intermediate temperature where alpha alumina is more soluble, but anode corrosion rates are still lower than high temperature operation might provide a reasonable compromise. Mechanical stirring in a separate part of the cell could provide much more rapid dissolution of the alumina, reduce the required overfeeding, and even dissolve some alpha alumina. Materials required for mechanical stirring apparatus would be more practical and reliable at lower cell operating temperatures.
- Electrolyte circulation was improved in these small cell tests to promote alumina dissolution, but circulation also increased aluminum droplet movement and this could have accelerated anode wear. A larger unit should allow an alumina feed region which is separate from the electrode areas, and this would help mitigate this problem. A highly agitated separate feed region would also help maintain saturation.
- The results suggest the possibility of two offsetting phenomena-corrosion of the anode versus oxidation of the anode. At higher temperatures and higher wear rates, a high resistance oxide layer does not build to a noticeable problem. At lower temperatures and wear rates, oxidation of the anode and high resistance layers are an obvious problem which may be compounded by difficulties in maintaining saturation. If the corrosion rate is reduced by metal phase purification, then the buildup of oxide accumulates and the resistance grows rapidly. One alternative explanation would blame removal of the anode from the cell which causes thermal shock and allows fume exposure. This certainly could have contributed to the resistance layer problem. Before Run 6, one of the

non-electrolysis tests, was done with the anode only exposed to the fume above the molten electrolyte. This anode grew and after removal from the cell had the highest resistance measured during this work.

- Operating at intermediate temperatures might eliminate the high resistance problem, but at a lower corrosion rates than occurs at typical Hall cell operating temperatures. Larger diameter anodes (relative to length) and/or higher conductivity anodes might reduce the resistance of these layers. The high resistance problem is reminiscent of a reverse bias on a semiconductor diode. It is known from another program that increasing the metal phase of a Cermet anode dramatically increases the electrical conductivity of the Cermet and the behavior becomes more metallic rather than semiconductive. Thus, a very conductive anode might reduce both the internal anode resistance and the resistance of the surface layer that forms at low temperature. A larger or more conductive anode would serve to flatten the current density and lower the voltage drop.
- The high anode resistance phenomena which is experienced at low temperature could also result from fluorination of the metal phase. Preferential elimination of this phase would reduce conductivity near the surface of the anode. This would be accelerated if the alumina concentration was significantly below saturation. Operating at an intermediate temperature and ratio might be useful for reducing both fluorination and dissolution of the anode if this explanation is correct.
- Obtaining realistic material balances was very difficult in these cells. The results shown in Table 6 for 100 hour run tests show a large scatter. Metal samples were difficult and even impossible to obtain during the long runs because of cathode deposits. One of the problems was the cathode connectors used in the longer runs in order to preclude the possibility of carbon. These connectors had significant axial heat losses which could have been a factor in depositing bath constituents on the cathode. The 100 hour runs had no connectors by using the graphite containment crucible as the cathode connector, but this provided some risk of carbon contamination. This occasionally was observed in the bath and removed by an oxygen bubbler. Another problem is the reaction of aluminum with the bath at startup to produce Na. This transient can significantly reduce the amount of aluminum present. The material balances obtained for the 100 hour runs do indicate Ni values lower than indicated by anode dimensional changes and Cu values that are higher and this is an indication of preferential metal phase attack.

Figure 30.

Cell Parameters 8th Run

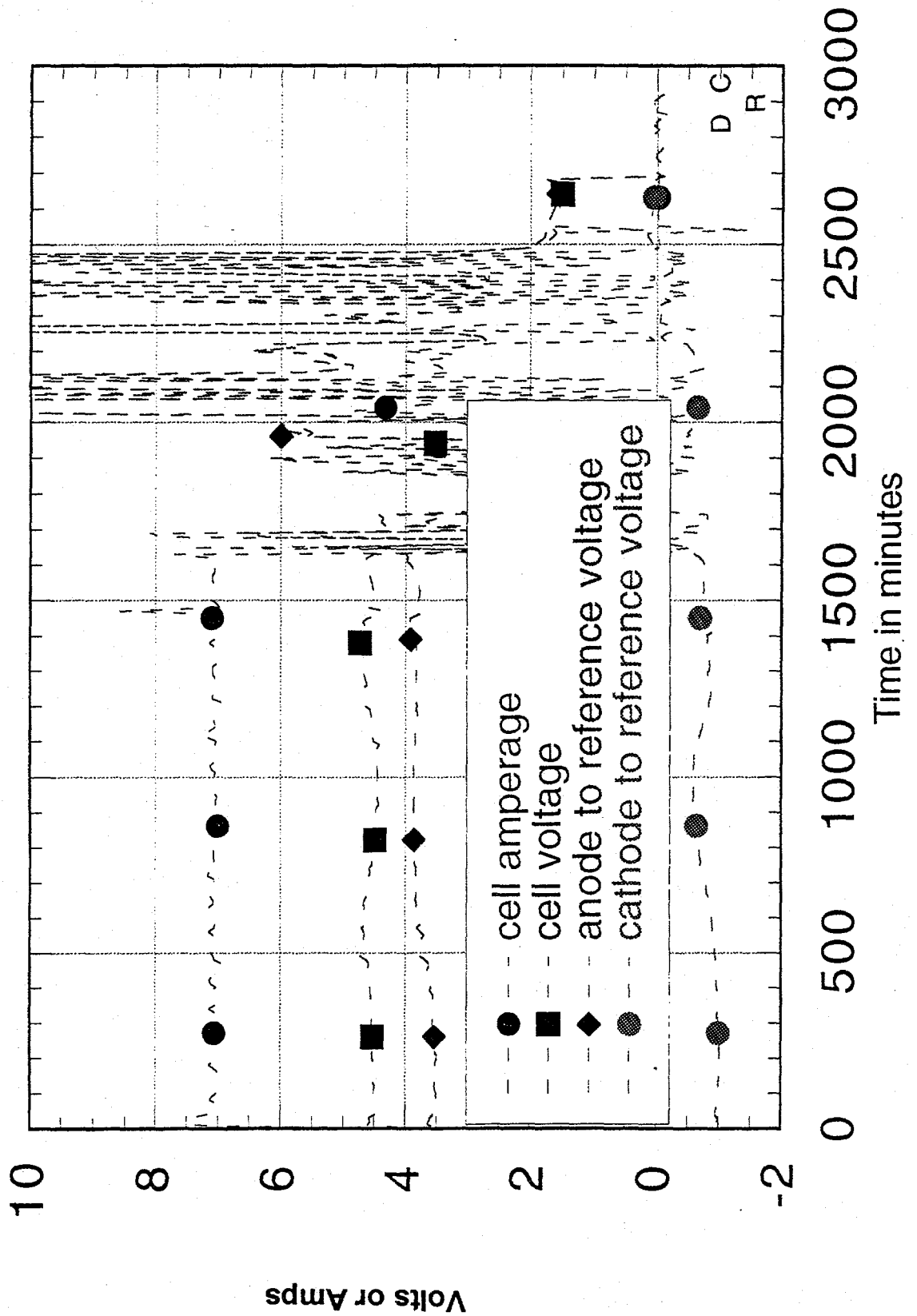
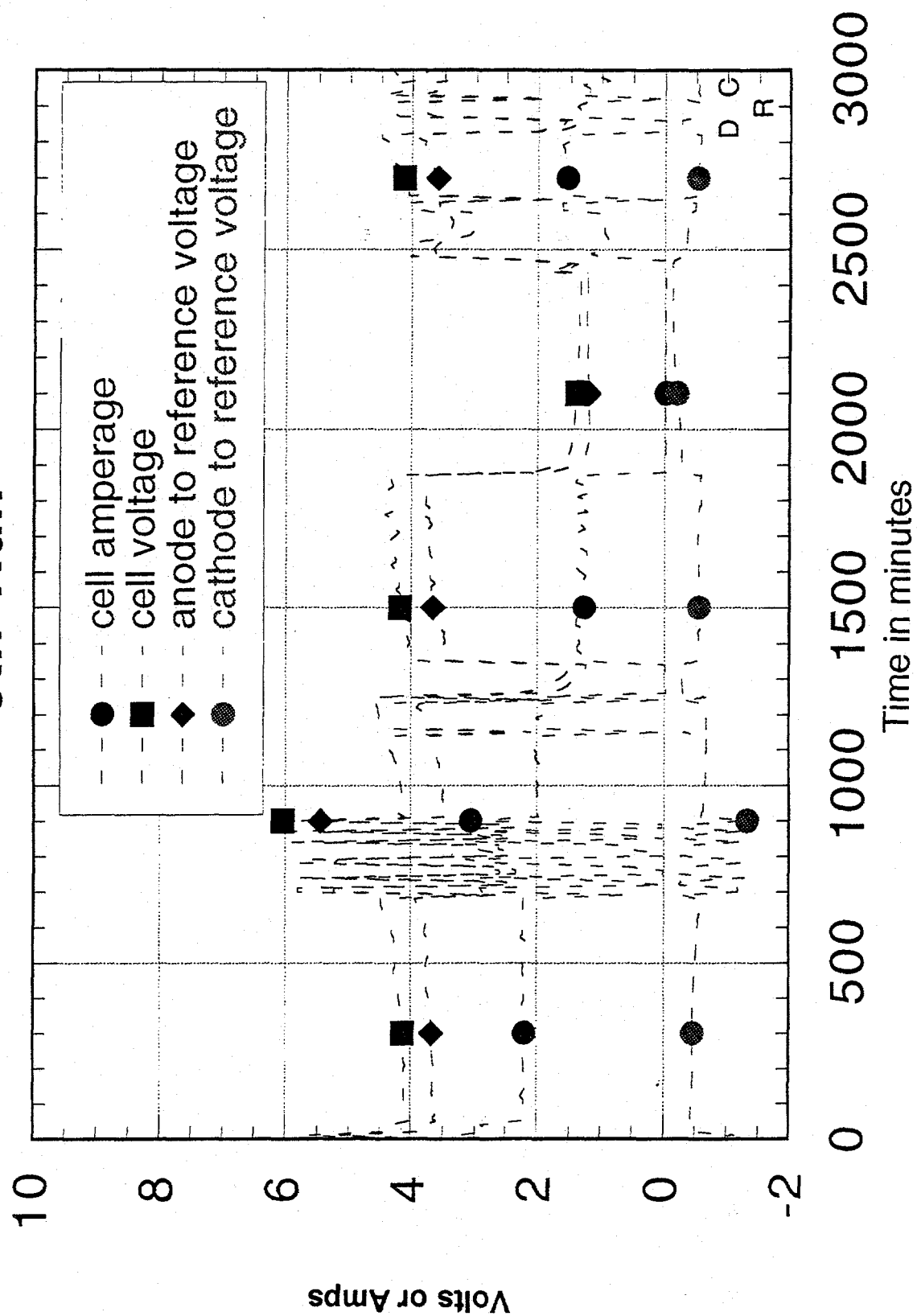


Figure 31

Cell Parameters 9th Run



Appendix I

FABRICATION OF 1/2" DIA. INERT ANODES

Following, are the procedures used in the fabrication and processing of the 1/2" diameter, graded connection, rounded bottom anodes, used in the DOE / Alcoa small Hall cell runs.

The powder used is a blend of as-received spray dried Stackpole 5324 powder** S#579617 and 17% -325 mesh screened 99.5% pure copper metal powder from Alfa cat.# 00094 Lot # B06A02.

These powders are weighed up in a glass jar, using 1000 gm batch weight, then the jar is placed in a Fisher Kendall mixer, and tumbled for at least four hours at 60 RPM.

The powder for the graded connection, is a blend of the 5324 powder + 17% copper (now referred to as "basic mix") with three different percentages of Inco HDNP nickel powder.

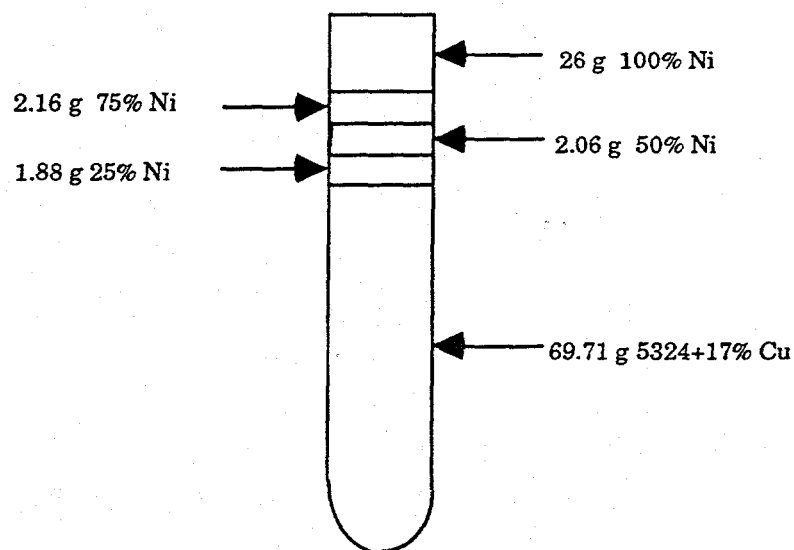
75% Ni

50% Ni

25% Ni

These powders are also blended in the Fisher Kendall mixer.

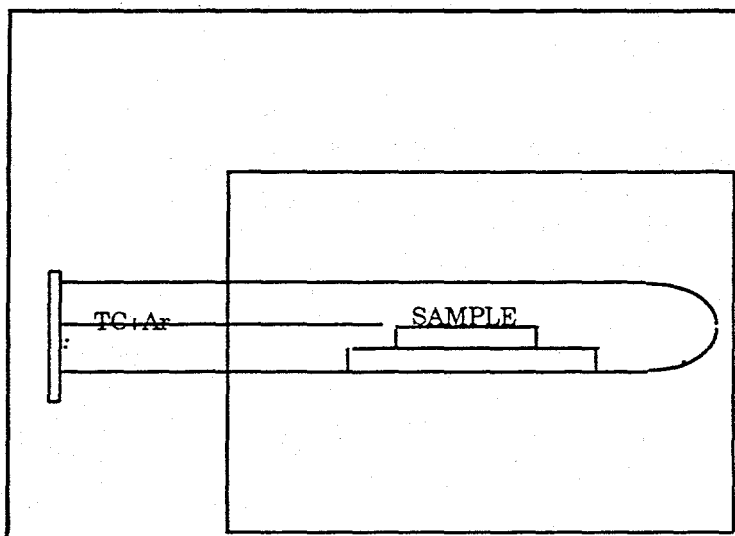
The powders are now blended and ready to be placed in the isostatic pressing molds. The bags, or molds, are ~11" long, and ~1" dia. They are purchased from the Trexler Rubber Co. in Ravenna, Ohio. The weights have all been previously calculated to give the size anode needed for the cell. The molds are filled placing the basic mix in the mold first, then using the nickel gradients, in order of increasing Ni content, finally going to 100% nickel, at the top. The powder lots are simply poured into the bag. Tapping the sides of the bag in between powder layers helps to level the top surfaces and settle the powder.



** 5324 powder is a blend of 51.7 wt.% NiO and 48.3 wt.% Fe₂O₃. Preferred source of NiO is Ceramic Color and Chemical N-139 (Green), surface area 2 m²/g. Preferred source of Fe₂O₃ is Pfizer Grade R-2900, surface area 9 m²/g. In previous programs, the powders were calcined at 900°C to form a (NiFe₂O₄+NiO) mixture, grinding the powder prior to spray drying in an open system with 1.5% PVA-PEG as the binder system. The spray dried agglomerates are ~40μ median particle size.

After the molds have been filled, a sealing closure and ring are placed in the end of the bag, and secured with a hose clamp. The filled molds are then placed into the press vessel and pressed to 20,000 psi. The press goes from 0 to 20,000 psi in approximately 3 minutes. They are then taken out of the press, dried off, then the part is removed, taking care not to get it wet.

The green part is now ready for sintering. It is first placed in an alumina tray, using 24 mesh calcined alumina as a bed grain. This alumina tray is then set on a "D" tube and slid into the 3" dia. tube of the Lindberg 1700°C tube furnace. The tray is positioned in the heat zone of the furnace. The tube is sealed, by bolting a stainless flange on, which has the argon inlet, exhaust, and thermocouple, running through it.



The following program is then started;

Room temp. to 400°C @ 144°/hr.
400°C to 1000°C @ 300°/hr.
2 hrs. @ 1000°C
1000°C to 1350°C @ 175°/hr.
2 hrs. @ 1350°C
1350°C to 1000°C @ 100° / hr.
Natural furnace cool to Room temp.

Note: Above temperatures are all internal tube temperatures.

The sample is removed when the furnace temp is below 150°C.

Industrial grade argon (20-80 ppm oxygen) is used at 2.0 LPM, as a purge gas throughout the entire run. An Ametek Thermox TM-1A instrument is used to determine oxygen content.

A small representative slug is sintered along with the anodes to be used for SEMs. This slug is the Stackpole 5324 + 17% Cu only powder, and is ~1" long. ASTM STD. C-20-83 test is used for determining the density, porosity and water absorption of the samples (full anode and the representative slug). The acceptable sample must have a porosity of < 0.03 % and water absorption < 0.01. The Cu content of the metal phase should be at least 81 wt.% by microprobe analysis.

Appendix II

SOP's for Cell Operation

Cell preparation and startup

- Inspect stainless steel shell and replace if necessary
- Clean bottom and add BB's to bottom for good electrical and thermal contact to graphite crucible.
- Coat outside of graphite crucible with BN paste including the top lip and 2" down the inside of the crucible to reduce air burning. The paste used is ZYP boron nitride lubricant. It is brushed on and dried for two hours at 125°C.
- Insert crucible into shell and then insert shell into furnace
- Notch alumina liner for bubbler and install inside crucible.
- Install alumina crucible and fill 1/8" gap with metal grade alumina powder. Make sure bottom is cell is vacuumed clean.
- Install downcomer tubes inside alumina crucible
- Tape in place with scotch tape.
- Position 30° angle toward center of cell.
- Position bubbler tube using lid.
- Add tabular alumina (~1000 gm. -3/+8 mesh) through funnel until crucible is about 3/4 full.
- Remove tape and add remaining tabular alumina.

2.3.2. Run preparation

- Load cell with aluminum pellets
Granular aluminum - 99.99%, grade GP Cast No. 31273 - 600 gm.
- Install lid and clamp.
- Add bath through funnel (2200 gm.)
- Install thermocouple and feed tube
Thermocouple - type K 18" - 1/8" diameter SS
Thermocouple sheath: 5/16" O.D. x 3/16" I.D. 99.8% alumina
- Install reference electrode
- Position to full depth initially to melt bath and aluminum inside electrode
- When cell is at temperature, adjust to 3/4" immersion.

- Charge alumina hopper with dry alumina
- Charge hopper with 550 gm. and blanket with argon.
- Hookup plumbing

Bubbler

- Connect tubing and set argon flow rate to 0.25 SCFH

Feeder

- Connect tygon tubing to feed tube
- Connect argon purge line
- Set argon flow rate to 1 SCFH.

Water lines

- Connect water lines to lid
- Adjust flow rate according to flow monitors
- Install insulation between furnace and top of shell
- Install blanket insulation between furnace and top of shell to insulate and seal top of furnace.

3.2. Start-up Operations

3.2.1. Drying alumina:

- Dry in oven @ 300°C for a minimum of 8 hours.

3.2.2. Bath Composition and preparation

Total Mix wt., 2200 g

wt% AlF_3 - 64%

wt% NaF - 36%

- Add 3.5 gm metal grade alumina to each 100 grams bath.
- Blend in ball mill type mixer.

3.2.3 Initial measurements

Anode dimensions

Total length of anode including rod to ± 0.0005 "

Diameter at selected locations

increments from end to 1 7/8"

and 90°

Metal heel weight

Alumina weight

Hopper + alumina

Net alumina

Tabular alumina weight

Bath mix weight

3.2.3. Start up sequence

- Set Furnace controller for heat up profile.

Heat up profile:

hour @ 60°C/hr

hour soak @ 680°C

+ hour @ 60°C/hr

< 8 hour soak @ 800°C

- Check bath temp and power draw at end of soak
- If power draw > 40% continue soak.
- If bath temp \neq 800°C reset furnace temp set point.
- Check and adjust levels

BATH LEVEL: Add make-up bath to adjust bath level to 1.25" over the alumina crucible.

Measure by freeze line on 1/8" tungsten rod. Record level and additions

METAL LEVEL: Record metal level. Measure by metal line on tungsten rod. (Note, due to capillary action the indicated metal level will be approximately 7/8" higher than the metal level. Since the amount of metal rise is nearly constant, the tungsten rod technique is useful for tracking relative changes in metal level.

TABULAR ALUMINA LEVEL: Measure with tungsten rod and record.

- Adjust reference electrode
- Raise electrode to 3/4" immersion
- Raise tungsten rod inside electrode to 0.5" from bottom of sheath.
- Adjust bath thermocouple to 1.5" immersion
- Increase bubbler flow to 1.0 SCFH Argon
- Take bath and metal samples
use 6 mm quartz tubing to aspirate samples.
samples for analytical

Bath

Ratio

AA for Fe, Ni, Cu, Al, Na to three decimal places

O₂

Metal

AA for Fe, Ni, Cu to three decimal places

- Install anode in lid and gradually lower into cell and hot zone.

Maximum lower rate 1"/5 minutes.

Set at 1.5" immersion in bath

- Hook up electrical connections

Anode

Cathode

Reference electrode

- Check temperature and correct furnace setpoint if necessary
- Turn on power supplies, IR switch, computer
- Execute program

Set feed rate

g/slug (depending on calibration data). (Don't forget to compensate for water in alumina.)

0.637 g/amp-hour (dry wt.)

- Set current for 7.5 amps
- Set print out time for every minute during start-up. Watch for reference electrode to equilibrate. This should occur in about 15 minutes to 1 hour. Then increase print time to normal every 15 minutes.
- Check feed counter to make sure feed rate is set properly. Adjust feed rate if necessary.

3.3. Steady State Operations

3.3.1. Operating targets and setpoints

Temperature	800°C
Ratio	0.56
Current	7.5 Amps
Anode immersion	1.5"
Current Density	1.0 A/in ²
Alumina Conc.	Saturation
Alumina Feed Rate	0.637 g/A-hr
Bath Level	1.25" over alumina crucible.
Bubbler Flow Rate	1.0 SCFH

3.3.2. Routine operations

Anode immersion Depth

Height between top of alumina crucible and bath
measure by freeze line on 1/8" tungsten rod.

Measuring bath and metal levels

Bath levels should be checked and logged at least every 24 hours.

Bath level is measured by the freeze line on a 1/8" tungsten rod. Measure to the nearest 1/16"

Measure tabular alumina depth

Difference between top of crucible and top of tabular alumina by 1/4" tungsten rod.

Adding make-up bath

Make-up bath should be added to maintain a level of 1.25" over the alumina crucible.

Volt-amp curves

Volt-amp curves are generated automatically by the computer once for every 60 sets of data logged. For instance if the logging rate is set for 1 minute, a volt-amp curve is generated once an hour. If the computer is set to log at 15 minute intervals a curve is generated every 15 hours.

The procedure used by the computer is to reduce the amps to the cell in six (6) 1-amp increments and record the voltage for 10 seconds and average the results.

Volt-amp curves can also be run on demand by entering the proper function key on the computer.

Feeder calibration

The feeder calibration is checked every 24 hours by the following procedure:

- Remove and weigh the feeder assembly
- Compute the weight of alumina fed to the cell by subtracting present feed assembly wt from the initial feeder assembly weight.
- Compute the weight per shot by dividing by the number of shots.

- If adjustments are required, input the new weight per shot to the computer.
- Calculate total demand for cell based on amp-hours and manually add additional feed shots.

Bath and metal samples

- Bath and metal samples should be taken at least once per day
- Use 6 mm high purity alumina tubing to aspirate samples.

Samples for analytical

Bath

Ratio

AA for Fe, Ni, Cu, Al, Na to three decimal places

O₂

Metal

AA for Fe, Ni, Cu to three decimal places

Visual observations

- Visual observations are important. Perform at least every 24 hours
- Visually inspect the internals of the cell through the lid for any changes whenever the cell is opened.
- During the 24 hour probing for metal and bath levels inspect the cell for the following :

Crusting on top of the metal pad

Buildup of muck on the bottom of the cell

Bubbler action

- During the 24 hour check of the feeder calibration, inspect the feed tube for plugging and rod out any blockages.
- Reference electrode stability should be monitored by observing long term drift in the cathode-to-reference voltage and by the zero current intercept of the cathode-to-reference signal during a volt-amp curve. If the drift gets too high, the reference electrode should be replaced.
- To replace the reference electrode use the following procedure:
- Preheat the new electrode in the warmup port to melt the aluminum and bath. This will take approximately 30 minutes.
- Lower the tungsten rod to 1/2" from the bottom of the alumina sheath.
- Pull out old reference electrode
- Quickly insert the newly preheated electrode to avoid thermal shock to the alumina tube.
- Inspect Bubbler tube. If necessary it must be rodded out with a tungsten rod.

Manual data logging - every 24 hours

amp-hour readings

feeder shot counts

Additions

Computer data logging

Reference electrode checks during V-I curve

Bubbler purge

IR changes

Alarm conditions and actions

3.4. Shutdown Operations

3.4.1. Shutdown Sequence after 100 hours

- Take final metal and bath samples
- Shut the feeder off
- Shut off current
- Stop the computer program
- Immediately, raise anode approx. 2 inches above bath
- Slowly raise anode the rest of the distance at a rate not to exceed 1"/5 minutes.
- Remove reference electrode and thermocouple
- To remove the anode from the cell use the following procedure:
 - Use a ring stand to support anode rod after unscrewing the swagelok fitting from the lid.
 - Continue to raise the anode until it is completely outside the cell and allow to cool in air for approximately 15 minutes.
- Remove lid
- Tapping cell and metal recovery
- Remove/stabilize chip well
- Pour into bath pan - let freeze
- Crush bath, remove and weigh metal

3.4.2. Final measurements

Anode dimensions

Total length of anode including rod to ± 0.0005 "

Diameter at selected locations
increments from end to $1 \frac{7}{8}$ "
and 90°

Metal heel weight

Alumina weight
Hopper + alumina
Net alumina

3.4.3. Calculations

Material balance on Fe, Ni, Cu

Current efficiency

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